

ISSN 0024-4902

Vol. 21, No. 3, May-June, 1986

January, 1987

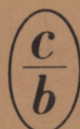
LTMRAR 21(3) 225-332 (1986)

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

Lithology and Mineral Resources is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Lithology and Mineral Resources is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Academy of Sciences of the USSR.

An agreement with the Copyright Agency of the USSR (VAAP) makes available both advance copies of the Russian journal and original glossy photographs and artwork. This serves to decrease the necessary time lag between publication of the original and publication of the translation and helps to improve the quality of the latter. The translation began with the first issue of the Russian journal.

Editorial Board of *Litologiya i Poleznye Iskopaemye*:

Editor: V. N. Kholodov

Associate Editors: I. V. Khvorova and B. M. Mikhailov

Secretary: G. Yu. Butuzova

G. A. Kaleda	A. V. Shcherbakov
A. G. Kossovskaya	Sv. A. Sidorenko
G. F. Krashenninnikov	A. S. Sokolov
A. P. Lisitsyn	V. A. Tenyakov
A. B. Ronov	P. P. Timofeev

Copyright ©1987, Plenum Publishing Corporation. *Lithology and Mineral Resources* participates in the Copyright Clearance Center (CCC) Transactional Reporting Service. The appearance of a code line at the bottom of the first page of an article in this journal indicates the copyright owner's consent that copies of the article may be made for personal or internal use. However, this consent is given on the condition that the copier pay the flat fee of \$12.50 per article (no additional per-page fees) directly to the Copyright Clearance Center, Inc., 27 Congress Street, Salem, Massachusetts 01970, for all copying not explicitly permitted by Sections 107 or 108 of the U.S. Copyright Law. The CCC is a nonprofit clearinghouse for the payment of photocopying fees by libraries and other users registered with the CCC. Therefore, this consent does not extend to other kinds of copying, such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale, nor to the reprinting of figures, tables, and text excerpts. 0024-4902/86/\$12.50

Consultants Bureau journals appear about six months after the publication of the original Russian issue. For bibliographic accuracy, the English issue published by Consultants Bureau carries the same number and date as the original Russian from which it was translated. For example, a Russian issue published in December will appear in a Consultants Bureau English translation about the following June, but the translation issue will carry the December date. When ordering any volume or particular issue of a Consultants Bureau journal, please specify the date and, where applicable, the volume and issue numbers of the original Russian. The material you will receive will be a translation of that Russian volume or issue.

Subscription (6 Issues)

Vol. 20: \$595 (domestic); \$660 (foreign) Single Issue: \$150
Vol. 21: \$645 (domestic); \$715 (foreign) Single Article: \$12.50

CONSULTANTS BUREAU, NEW YORK AND LONDON



233 Spring Street
New York, New York 10013

Published bimonthly, consisting of Volume 20 issues 3 through 6 and Volume 21 issues 1 and 2. Subscription price for Volume 20 is \$595, and for Volume 21 \$645. Second-class postage paid at Jamaica, New York 11431.

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

POSTMASTER: Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

January, 1987

Volume 21, Number 3

May-June, 1986

CONTENTS

Engl./Russ.

Pollen and Spore Distribution in Bottom Sediments of the Black Sea - A. V. Komarov.....	225	3
Behavior of Lanthanides and Yttrium during Rock Weathering - T. F. Boiko, Yu. P. Sotskov, and M. M. Maeva.....	234	12
Mineral Composition of Upper Visean Deposits of the Northern Dnieper-Donets Basin - E. Z. Ivanova.....	247	27
Trace Elements in Allophane-Gibbsite Rocks of Don-Medveditsa Dislocations - B. F. Saltykov.....	251	32
Lower Proterozoic Cupriferous Formations of the Ugui Frough, South Yakutia, and Their Correlation with the Udokan Complex - Yu. V. Davydov.....	260	44
Manganese Prospects of Rogachev-Severotaininsk Area of Novaya Zemlya - S. K. Voyakovskii.....	273	59
Apatitic Sandstones in the Headwaters of the Seligdar River, South Yakutia (Aldan Crystalline Shield) - A. G. Bulakh and V. N. Shvanov.....	282	70
Primary Structures of Sulfur Ores and Their Classification - S. K. Kropacheva, L. S. Sonkin, and V. E. Ponomarev.....	288	78
Lithologic Features of Carbonate Deposits of the Eastern Caspian Depression in Conjunction with Their Oil and Gas Prospects - Yu. A. Ivanov and S. M. Blank.....	300	91
Diagenesis and Dolomitization of Carbonate-Sulfate Jurassic and Cretaceous in Daghestan - I. E. Efendiev.....	309	103
Lithological-Facies Features of Upper Riphean Deposits of the Southern Urals. Communication 2. Facies and Paleogeographies during the Deposition of the Terrigenous-Carbonate Deposits of the Upper Part of the Zil'merdaksk Suite - A. V. Maslov.....	320	116
METHODS		
A Means of Sampling Suspended Sediments in Bottom Waters on Any Part of the Shelf - R. D. Kos'yan and A. P. Filippov.....	328	135

The Russian press date (podpisano k pechati) of this issue was 5/21/1986.
Publication therefore did not occur prior to this date, but must be assumed
to have taken place reasonably soon thereafter.

POLLEN AND SPORE DISTRIBUTION IN BOTTOM SEDIMENTS OF THE BLACK SEA

A. V. Komarov

UDC 550.7:551.35(262.5)

Palynologic studies of Recent and Upper Quaternary sediments, aerosols, and the river and sea suspended matter of the Black Sea basin have established the main factors determining the quantitative distribution of pollen and spores in bottom sediments: geographical distribution of the vegetable cover; physical and morphological parameters of pollen and spores; the distance to the plant habitats; and the correlation between the pollen and spore concentration peaks and regions with low sedimentation rates. The variability of pollen and spore concentration in the Black Sea is demonstrated in the paper to be controlled by the wind and hydrodynamic conditions in the basin, as well as the granulometric differentiation of sedimentary matter.

Palynologic studies of Recent sea-floor sediments reveal noticeable differences in the distribution and accumulation of pollen and spores in shallow [1, 2, 5, 12, 26, 30] and deep [1, 2, 6-10, 21, 25] basins. Pollen and spores are distributed in deep-sea basins in different patterns, especially in inland seas. This is confirmed, in particular, by the findings obtained by us in the Black Sea and a correlation of these data with those for other basins. These results are analyzed in the present paper.

MATERIALS AND METHODS

The palynologic studies were done on 250 specimens of sea-floor sediments, collected at more than 200 sites [6, 7]. The studies determined the basic material and genetic types of Recent sediments [18] and morphostructural elements of the sea-floor topography: shelf, continental slope, and abyssal plane. The results of studies of 16 characteristic columns [16-18] from the Upper Quaternary in the Black Sea (up to 7 m thick, 350 specimens) have been analyzed, as well as the profiles investigated by Soviet [10] and foreign [27, 29, 31] authors.

The pollen and spore concentrations were estimated per 1 g of dry natural sediment, according to the formula [4]

$$K = \frac{3.3A \cdot B}{C \cdot D},$$

where K is the absolute number of pollen grains and spores (concentration); 3.3, a constant (the number of drops in 1 ml of the dropper used); A, volume of the maceration product, ml; B, number of grains counted in the prepared specimen; C, number of drops in which the counts were done; and D, weighted amount of dry natural sediment specimen, g.

In order to compare these data with the estimates obtained by foreign authors [21, 24, 25, 29, 30], we recalculated the pollen and spore concentrations by using the formula [30]

$$K = (A \cdot B) / (C \cdot D),$$

where K is the absolute number of pollen grains and spores (concentration); A, gross weight of the residue of maceration and glycerine-gel emulsion, g; B, number of pollen grains and spores in the prepared specimen; C, gross weight of the product of maceration and glycerine-gel emulsion in the preparation, g; and D, weight of the dry sediment specimen, g.

Southern Branch, Institute of Oceanology, Academy of Sciences of the USSR, Gelendzhik. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 3-11, May-June, 1986. Original article submitted June 7, 1985.

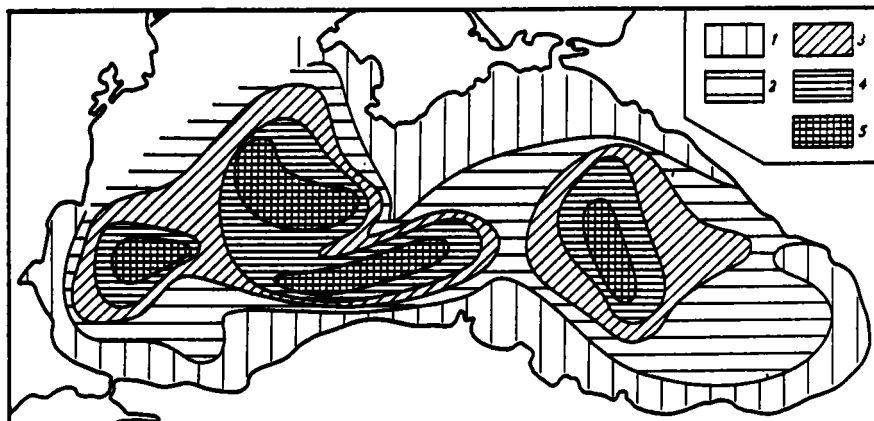


Fig. 1. Total pollen and spore concentration in surface layer (0-1 cm) of Recent sediments of the Black Sea. Contents, 1000 ind./1 g of dry natural sediment: 1) >1; 2) 1-5; 3) 5-50; 4) 50-100; 5) 100-200.

TABLE 1. Quantitative Distribution of Pollen and Spores in the Surface Layer (0-1 cm) of Recent Black Sea Sediments and in Aerosols

Sea depth, m	Seafloor area, km ² [3]	Mean concn. of pollen grains and spores			Abs. wt. of pollen and spores, mg/cm ² *	Accumulation time, years
		%	10 ³ equiv./g	10 ³ equiv./cm ²		
0-100	101 452	24,1	0,5	0,125	0,003	0,25
100-500	26 010	8,2	4,0	1,0	0,03	2,5
500-1500	54 700	13,0	21,0	5,25	0,15	12,5
1500-2000	86 571	20,6	30,0	7,5	0,22	18,3
2000-2245	151 592	36,1	160,0	40,0	1,20	100,0
Aerosol	420 325	100,0	—	0,398	0,012	1,0

*In estimates of absolute weight of pollen and spores, the mean weight of *Pinus silvestris*, $30.08 \cdot 10^{-9}$ g is [29] is used as a basis; it is the most frequent pollen in Recent Black sediments.

The calculations based on the two formulas, and performed for the same specimens indicated a good convergence, making it possible to compare the findings for the Black Sea with the data obtained in other basins.

RESULTS

Pollen and spore concentration in the surface layer (0-1 cm) of Recent Black Sea sediments was the highest (Fig. 1, Table 1) compared with other inland seas and oceans covered in the cumulative data survey in [2].

A comparison of the distribution patterns of general pollen and spore concentrations (see Fig. 1) and material-genetic types of Recent sediments [28] indicated that biogenic-terrigenous calcareous (CaCO₃ 30-50%) pelitic ooze in deep-sea horizons has the highest pollen and spore concentrations. The maximum pollen and spore concentrations tended to occur in the fields of biogenic (coccolithic) high-calcareous (CaCO₃ < 50%) ooze with a high content of pelitic fraction and predominant grain size of 0.002-0.005 mm and less. The sediments in this sea region are of a medium sorting ($S_0 = 2$) and are confined to halistatic regions of the abyssal plane.

High pollen and spore concentrations (100,000-160,000 individuals/g) have also been obtained here by Koreneva, Udintseva [10], and Traverse [29].

What factors are responsible for this singularity in the pollen and spore distribution? The answer to this question is provided by the palynological study of aerosols and river suspended matter [7].

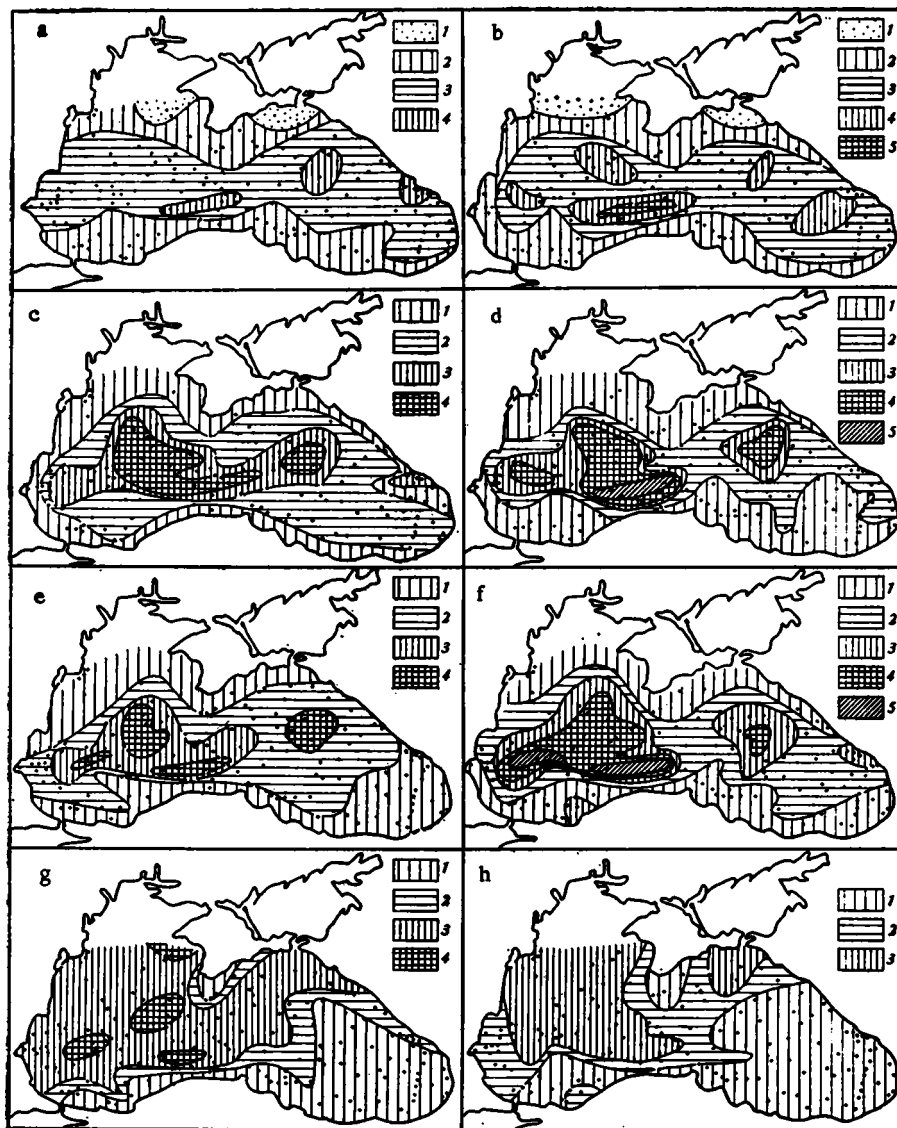
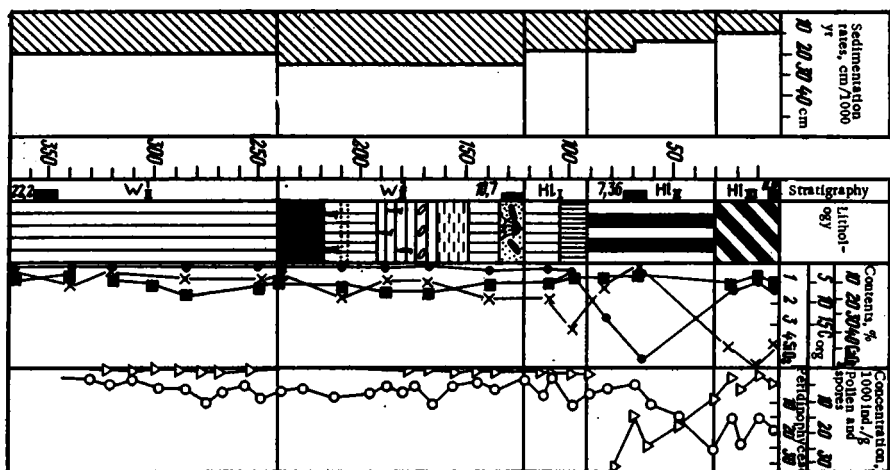


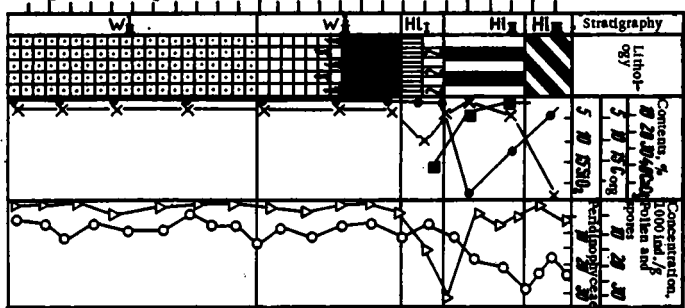
Fig. 2. Quantitative distribution of predominant pollen types in Recent Black Sea sediments: 1000 ind./1 g of dry natural sediment: a) *Abies* (1 – absent; 2 – 0.01-0.1; 3 – 0.1-0.5; 4 – 0.5-1); b) *Picea* (1 – absent; 2 – 0.01-0.1; 3 – 0.1-0.5; 4 – 0.5-1; 5 – >1); c) *Pinus* (1 – 0.05-1; 2 – 1-5; 3 – 5-10; 4 – >10); d) *Fagus* (1 – 0.05-0.5; 2 – 0.5-1; 3 – 1-3; 4 – 3-5; 5 – >5); e) *Quercus* (1 – 0.05-1; 2 – 1-5; 3 – 5-10; 4 – >10); f) *Carpinus* (1 – 0.05-0.5; 2 – 0.5-1; 3 – 1-2; 4 – 3-5; 5 – >5); g) *Chenopodiaceae* (1 – 0.03-0.5; 2 – 0.5-1; 3 – 1-5; 4 – >5); h) *Artemisia* (1 – 0.02-1; 2 – 1-2; 3 – 2-5).

Pollen and spore concentrations in aerosol specimens collected above the Black Sea surface is, on average, 398 counts per cm^2 [7]. The seasonal influx of pollen and spores by aerial routes into the Black Sea has been estimated at $16.7 \cdot 10^{17}$ ind. For comparison, the "pollen shower" above the Azov Sea is $12 \cdot 10^{16}$, the Caspian Sea $16 \cdot 10^{16}$, the Aral Sea $11 \cdot 10^{16}$ [1], and the western Atlantic $15 \cdot 10^{18}$ ind. [24]. In several basins, it has been determined that the bulk of pollen and spores is transported in an aerosol form. In particular, the Baltic Sea receives 98.5% of pollen and spores by this route [5], the Aral Sea 97, the Azov Sea 99, and the Caspian Sea 98% [1, 2]. The river suspended matter brings into the seas 1-3% of the total amount of pollen and spores, i.e., about one-hundredth of this amount. No pollen and spores have been found in the suspended matter of the northern parts of the Black Sea [7], although the specimens were collected during the blossoming season of most trees, shrubs, and grasses.

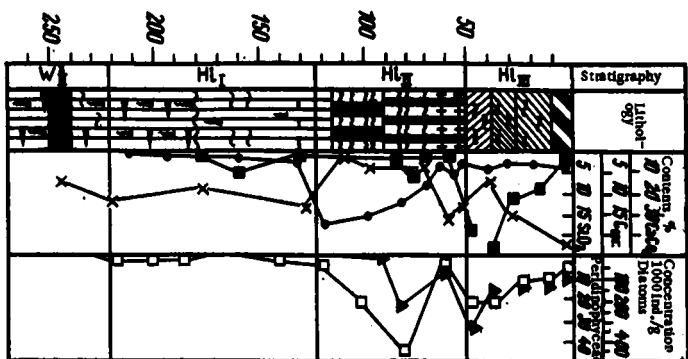
Site 1853 depth 2075 m [187]



Site 4753 depth 750 m; Site 1445 [177]



Site 1853 depth 520 m [207]



Site 4750 depth 2785 m; Site 1474 [22, 28, 317]

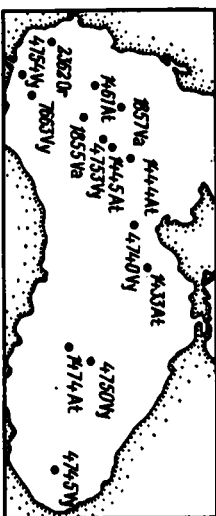
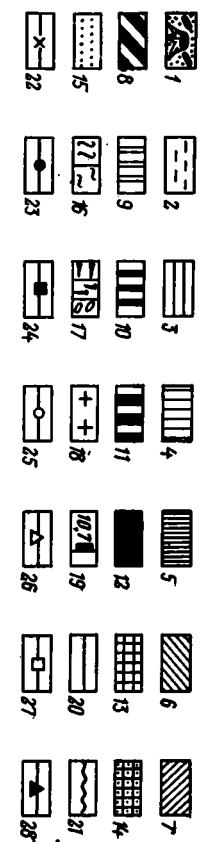
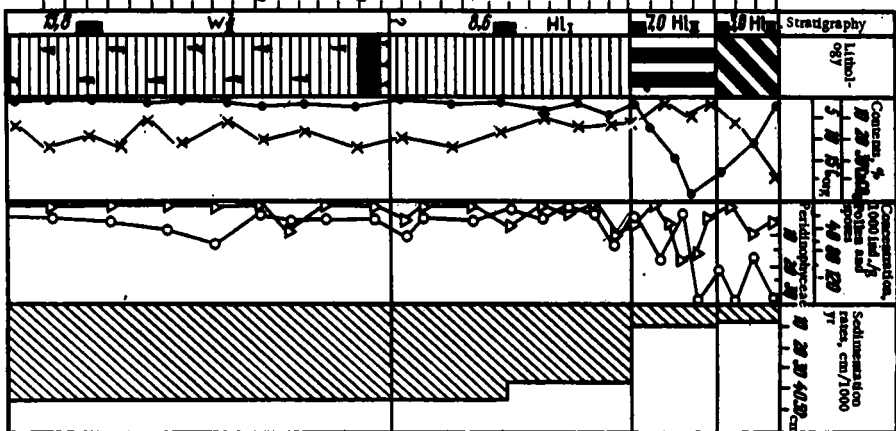


Fig. 3. Correlations of the concentrations of pollen and spores, diatoms, silicoflagellates, and *Peridinophyceae* with the contents of CaCO_3 , Corg, SiO_2 (amorph), and sedimentation rates in the Upper Quaternary profiles of Black Sea sediments: Lithology: 1) terrigenous sand-silt sediments with lignite fragments; 2) terrigenous small-silt ooze; 3) carbonate-free clay ooze; 4) low-calcareous (CaCO_3 10-30%) clayey and silt-clayey ooze, poor in organic matter (gray and bluish-gray); 5) calcareous-clayey (CaCO_3 30-50%) ooze, poor in organic matter (bluish-gray); 6) low-silicic diatom ooze (calcareous); 7) low-silicic diatom ooze (low-calcareous); 8) high-calcareous coccolithic ooze (CaCO_3 > 50%; Corg 5-6%); 9) carbonate-free and low-calcareous pelitic ooze (Corg 2.75-5.5%); 10) sapropel carbonate-free pelitic microstratified ooze (CaCO_3 < 10%; Corg 5.5-16.5%); 11) sapropel-clay and clay-sapropel ooze (CaCO_3 10-30%; Corg 5.5-16.5% and more); 12) carbonate-free and low-calcareous clay ooze enriched in hydrotroilite (black); 13) carbonate-free striated-maculose clay (alternation of gray, reddish, and brown strips); 14) same, but with thin (a few centimeters) interlayers of terrigenous siltstone; 15) thin interlayers of terrigenous siltstone; 16) diatom-clay ooze (SiO_2 (amorph) 10-30%), microstratified greenish-brown (a) and microlayers and thin seams of diatom ooze (b); 17) irregular discontinuous interlayers of hydrotroilite (a), smears of hydrotroilite (b) and lenses of hard clayey greenish-gray ooze (c); 18) microlayers of coccolithic ooze; 19) radiocarbon datings. Discontinuity boundaries: 20) sharp, even; 21) blurred. Distribution of principal components: 22) CaCO_3 ; 23) Corg; 24) SiO_2 , 25) pollen and spores; 26) *Peridinophyceae*; 27) diatoms; 28) silicoflagellates. Stratigraphic horizons: W_{II}^I) early euxinic (15.5-25.0 thousand years ago); W_{II}^I) middle-neoeuxinic (10.5-15.5 thousand years ago); H_{II}) late neoeuxinic (7.0-8.0-10.5 thousand years ago); H_{II}) ancient Black Sea (3.0-7.0-8.0 thousand years ago); H_{III}) late Black Sea (0.0-3.0 thousand years ago). Indices of research vessels. Va) Akademik S. Vavilov, Or) Akademik L. Orbeli, Vy) Vytiaz, At) Atlantis-II.

The principal factor determining the distribution of pollen and spores in the Black Sea is, thus, the transportation of this material by aerial routes during the maximum pollen productivity of the vegetation on the shore. This conclusion is confirmed by the inverse correlation of the absolute weights of pollen and spore material (see Table 1) and the absolute weights of terrigenous matter [13] in the Recent sediments of the Black Sea.

The maximum values of absolute weights of terrigenous sedimentary matter tend to be found in the peripheral parts of the sea, while the largest amounts of pollen and spores are found in central areas of the basin. The relatively high pollen and spore content has also been observed in sea-floor sediments, tending toward undrained parts of the Black Sea coast.

The range to which the pollen and spores are transported is largely determined by the morphology, size, and specific weight of the grains (Fig. 2, Table 2). The "air bags" in the pollen of the genera *Abies*, *Picea*, and *Pinus* separate them into a morphological group. A comparison of the distributions of the pollen of these genera (see Fig. 2) suggest that the variations in their content can be attributed to the size, mean weight, and the speed of fall in calm air (see Table 2). The maximum susceptibility to air flow transport from habitats to the sedimentation basin is exhibited by *Pinus* pollen, which weighs just one-tenth that of *Abies*, and one-third that of *Picea*. The mean length of a *Pinus* pollen grain is about one-third that of *Abies* and one-half that of *Picea*. The speed of fall in the air of *Pinus* pollen is accordingly much slower than that of *Abies* and *Picea*. Given the high pollen productivity of *Pinus*, its pollen can be carried to large distances from the habitats in the lower layers of the troposphere (see Table 2).

Similar distribution features of *Pinus* pollen have been observed in the Mediterranean [1], the Sea of Okhotsk [8], the Baltic Sea [5, 26], the Gulf of California [21], the Pacific [9, 25], and near the Bahama bank in the Atlantic [30]. The distribution of the concentrations of pollen of these and other genera (see Fig. 2) emphasizes the correlation with the physicomorphological parameters and the specific air transport routes in the Black Sea.

Pollen and spore concentrations in sediments correlate with the contribution of the species, genus, and family to the vegetation on the shore. The species of *Pinus*, *Quercus*, *Carpinus*, and *Alnus* often form the wooded tracts abutting the coast, while the habitats of *Abies*, *Picea*, and *Fagus* are more limited. These species are confined to particular altitude and climatic zones, which sometimes are remote from the sea. As a result, the pollen concentrations of these genera in sediments are much lower (see Fig. 2, Table 2).

The maximum pollen and spore concentrations in the sediments of halistatic areas are due to granulometric differentiation of sedimentary matter in the Black Sea, as well as to the long-range aeolian transport.

As the pollen and spores precipitate from aerosol onto the sea surface, they undergo the actions of hydrodynamic and sedimentation processes. The permanent cyclonic currents bring the pollen and spores out of the sea perimeter into the middle of the basin, along with the light subfraction of small-silt matter and pelite. For this reason, the pelitic fraction in the middle sea regions is enriched in pollen and spores. The confinement of the maximum pollen and spore concentration to sediments with high organic and carbonate contents is not genetic, but purely formal, due to the fact that high-carbonate and high-organic coccolithic ooze is present in halistatic regions. This is confirmed by the distribution of pollen and spore concentrations in Upper Quaternary profiles (Fig. 3, Table 3).

The ancient Black Sea sediments (Middle Holocene) that have the highest organic contents display much lower pollen and spore concentrations than the late Black Sea sediments (Late Holocene) and Recent layers in the Black Sea.

In the deep-sea parts, the Recent sediments have the highest pollen and spore concentrations, owing to slow sedimentation rates, especially in halistases and the intensive supply of this material from the shore, because the distance from the shore to the middle of the sea is not large — 100–200 km.

The absolute weights of pollen and spores are 1.2–1.5 mg/cm² for sedimentation rates of 8–10 cm/1000 years [15, 19], and are typical for the middle of the basin. In peripheral zones, the absolute weights of pollen and spore material drop to 0.03–0.003 mg/cm², while sedimentation rates are much higher, up to 90 cm/1000 years. The data of Tables 1 and 3 show that the absolute weights of pollen and spores in the deep-sea sediments are controlled by sedimentation rates.

TABLE 2. Correlation of the Concentration of Pollen Predominant in Sediments with the Physical-Morphological Parameters and Features of Air Transport in the Black Sea [11, 23]

Pollen (genus)	Pollen concns., grains/1 g of sediment	Mean pollen length, μm	Mean pollen weight, 10^{-9} g	Speed of free fall in the air, cm/sec	Transportation route	Fraction of sediment	Transportation range, km	Time airborne
<i>Abies</i>	12—1 400	143,0	328,0	38,71	Transportation in low tropospheric layer	Small sand	10—100	Seconds, hours, rarely days
<i>Picea</i>	7—3 070	102,0	93,2	6,84	The same	The same	10—100	The same
<i>Pinus</i>	46—40 000	59,0	30,08	3,69	Transportation in low tropospheric layer	Coarse silt	100—1000	Hours, days
<i>Fagus</i>	40—7 640	53,2	—	—	The same	The same	100—1000	"
<i>Carpinus</i>	66—12 185	35,0	22,0	6,79	"	Small silt	100—1000	"
<i>Tilia</i>	5—2 590	31,0	21,7	3,24	"	The same	100—1000	"
<i>Quercus</i>	80—31 960	24,8	18,16	3,96	"	"	100—1000	"
<i>Corylus</i>	30—6 000	24,2	9,45	2,90	"	"	100—1000	"
<i>Alnus</i>	38—26 200	24,6	9,37	2,77	"	"	100—1000	"

TABLE 3. Correlations of the Concentrations of Pollen and Spores, Diatoms, Silicoflagellates, and *Peridinophytaceae* with Contents of Organic Matter, Carbonates, and Sedimentation Rate*

Horizon	Concentration						Sedimentation rate, cm/1000 yr	
	pollen and spores	peridinophytaceae	diatoms	silicoflagellates	C	CaCO ₃	entire basin	halistases
	late Black Sea		ancient Black Sea		%			
Ancient Black Sea	100—200	7—9	50—150	10—30	2,54	26,3	6,0—61,5	10
Late neoeuxinic	7—100	10—25	150—447	5—25	11,55	13,2	1,2—90,0	30
Middle neoeuxinic	5—20	5—10	0—10	—	0,61	16,0	5,5—67,8	40
Early neoeuxinic	0,6—10	0,5—2	—	—	0,61	16,0	—	60—70
Surozh	0,5—7,0	0,2—0,5	—	—	0,61	16,0	—	70
	10—20	—	—	—	1,5	15,0	—	40—50

*Data reported in [6, 7, 14—16, 19, 20—22, 27, 29 31].

The principal factors responsible for the variability of pollen and spore concentration in the bottom sediments of the Black Sea are the following:

the density of vegetation, geographical occurrence and participation of species, genera, and families whose pollen and spores concentrate in sea-floor sediments;

the volumes of pollen and spore and their susceptibility for air transport due to pollen productivity, morphology, size, and weight of pollen and spore grains, and their speed of fall in calm air;

the distance from the habitats of the particular species, genera, and families to the Black Sea water body (the maximum pollen and spore concentrations are observed for those plants growing close to the shore);

the maximum pollen and spore accumulation in deep-sea bottom sediments is observed in regions with low sedimentation rate and intensive supply of pollen and spore material from the coast.

The variability of pollen and spore concentrations in the Black Sea basin is controlled by:

wind conditions during the maximum pollen productivity season of coastal vegetation. The pollen and spore are supplied mainly in spring, summer, and early-fall seasons. The amounts of pollen and spore in aerosol have been observed to rise sharply in cases of rapid wind currents. In the suspended matter in the rivers of the Caucasian, Crimean, and Ukrainian catchment areas, no pollen and spores have been observed, although the suspension specimens were collected during the blossoming season of most plants on the shore;

the hydrodynamic conditions in the Black Sea (the velocity and direction of surface currents and, in estuarian areas, the speed of the river stream) and the mixing of the water mass;

granulometric differentiation of sedimentary matter in the surface water layer. The differentiation and accumulation of pollen and spores are distributed similar to accumulation of sedimentary matter; as a result, the fields of maximum concentration of pollen and spores coincide spatially with the material-genetic types of sediments characterized by a high content of pelitic fraction, organic matter, and carbonates.

LITERATURE CITED

1. V. A. Vronskii, *Marinopalynology of Southern Seas* [in Russian], Rostov State Univ., Rostov-on-Don (1976).
2. V. A. Vronskii, "Pollen and spore concentration in Recent continental and marine sediments," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 12 (1981).
3. V. P. Goncharov, Yu. P. Neprochnov, and A. F. Neprochnova, *Seafloor Relief and the Deep Structures of the Black Sea Basin* [in Russian], Nauka, Moscow (1972).
4. M. V. Kabailene, *The Formation of Pollen Spectra and the Methods for Reconstruction of Paleovegetation* [in Russian], Mintis, Vilnius (1969).
5. M. V. Kabailene, "Aspects of formation of pollen spectra in marine basins," in: *Palynology in the USSR (1976-1980)* [in Russian], Nauka, Moscow (1980).
6. A. V. Komarov, "Palynological complexes of Recent deep-sea sediments of the Black Sea," in: *Palynology in the USSR (1976-180)* [in Russian], Nauka, Moscow (1980).
7. A. V. Komarov, "Pollen and spore accumulation in Black Sea sediments and the paleogeography of the basin during the Late Quaternary," in: *The Geology of Seas and Oceans* [in Russian], Vol. 1, Akad. Nauk SSSR (1982), pp. 44-46.
8. E. V. Koreneva, "Spore and pollen analysis of the bottom sediments of the Okhotsk Sea," *Tr. Int. Okeanol. Akad. Nauk SSSR*, 44-46 (1982).
9. E. V. Koreneva, *Spores and Pollen from Seafloor Sediments in the Western Pacific* [in Russian], Nauka, Moscow (1964).
10. E. V. Koreneva and O. G. Udintseva, "Palynologic study of two cores from Black Sea bottom sediments," in: *Paleontological Substantiation of the Anthropogene Stratigraphy: Proceedings of the 10th INQUA Congress* [in Russian], Moscow (1977), pp. 129-150.
11. A. P. Lisitsyn, *Processes of Oceanic Sedimentation* [in Russian], Nauka, Moscow (1978).
12. E. S. Malyasova, "The formation of the spore and pollen spectra in the surface layer of the Barents Sea sediments," in: *Palynology in the USSR (1976-1980)* [in Russian], Nauka, Moscow (1980), pp. 107-109.

13. N. M. Strakhov, "Sedimentation in the Black Sea," in: *Sediment Formation in Recent Basins* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1954), pp. 81-136.
14. N. M. Strakhov, "Geochemical evolution of the Black Sea during the Holocene," *Litol. Polezn. Iskop.*, No. 3, 3-17 (1971).
15. K. M. Shimkus, E. M. Emel'yanov, and É. S. Trimonis, "Seafloor sediments and features of the Late Quaternary history of the Black Sea," in: *Earth Crust and Elements of the Late Quaternary History of the Black Sea* [in Russian], Nauka, Moscow (1975), pp. 138-163.
16. K. M. Shimkus and A. V. Komarov, "Pleistocene deposits on the slopes of the Black Sea basin and paleogeographic characteristics," *Peribalticum, Ossolineum*, II, 49-54 (1982).
17. K. M. Shimkus, A. V. Komarov, B. Baishvilene, and N. Savukinene, "Stratigraphy of deep-water sediments of the Black Sea basin based on palynologic data and some paleogeographic conclusions," in: *Geological and Geophysical Studies of the Mediterranean and the Black Sea* [in Russian], Nauka, Moscow (1979), pp. 53-70.
18. K. M. Shimkus, A. V. Komarov, and I. V. Grakova, "Stratigraphy of deep-water Upper Quaternary Black Sea sediments," *Okeanologiya*, 17, No. 4, 675 (1977).
19. K. M. Shimkus, A. Yu. Mitropol'skii, and N. N. Kovalyuk, "New data on the geochronology of the bottom sediments of the Black Sea and sedimentation rates," *Geol. Zh.*, 38, No. 4, 44-53 (1978).
20. K. M. Shimkus, V. V. Mukhina, and É. S. Trimonis, "The contribution of diatoms to Late Quaternary sedimentation in the Black Sea," *Okeanologiya*, 13, No. 6, 1066 (1973).
21. A. T. Cross, G. G. Thompson, and G. B. Zaitzeff, "Source and distribution of palynomorphs in bottom sediments, southern part of Gulf of California," *Marine Geol.*, 4, No. 6, 467-524 (1966).
22. E. T. Degens and D. A. Ross, "Chronology of the Black Sea over the last 25,000 years," *Chem. Geol.*, 10, No. 1, 1-16 (1972).
23. J. Dyakowska and J. Zurzicki, *Bull. Acad. Polon. Sci.*, 2, No. 1, 11-17 (1959).
24. J. J. Groot and C. R. Groot, "Marine palynology: Possibilities, limitations, problems," *Marine Geol.*, 4, No. 6, 387-395 (1966).
25. L. Heusser and W. L. Balsam, *Quatern. Res.*, 7, 45-62 (1978).
26. K. Lubliner-Mianowska, "Pollen analysis of surface samples of bottom sediments in the Bay of Gdansk," *Acta Soc. Botan. Polon.*, 31, 305-312 (1962).
27. S. Roman, "Polynoplanktologic analysis of some Black Sea cores," in: *The Black Sea: Geol., Chem., Biol. Am. Assoc. Petrol. Geol.* (1974), pp. 396-410.
28. K. M. Shimkus and E. S. Trimonis, "Modern sedimentation in the Black Sea," in: *The Black Sea: Geology, Chemistry, Biology, Am. Assoc. Petrol. Geol.* (1974), pp. 249-278.
29. A. Traverse, "Polynologic Investigation of two Black Sea Cores," in: *The Black Sea: Geology, Chemistry, Biology, Am. Assoc. Petrol. Geol.* (1974), pp. 381-388.
30. A. Traverse and R. M. Ginsburg, "Palynology of the surface sediments of Great Bahama Bank, as related to water movement and sedimentation," *Marine Geol.*, 4, No. 6, 417-459 (1966).
31. D. Wall and B. Dale, "Dinoflagellates in Late Quaternary deep-water sediments of Black Sea," in: *The Black Sea: Geology, Chemistry, Biology, Amer. Assoc. Petrol. Geol.* (1974), pp. 364-380.

The mobility of individual La-elements and Yttrium was investigated in weathering horizons of various rocks. The degree and directional patterns of change of rare-earth element fractions was studied during processes that involved hypergenetic changes of the substrate. Concentration potentials of lanthanides and Y in weathering horizons are also discussed, as well as their migration activity in the weathering cycle.

Typical aspects of rare-earth element (REE) composition in sedimentary matter may be investigated while solving genetic problems of sediment accumulation in continental and in oceanic settings. One must know the composition of lanthanides in rock weathering products that later are introduced into depositional basins. Data on the mobility of REE and Y during the weathering processes allow estimation of their distribution in various hypergenetic substances. This is important in particular in geochemical exploration and in estimation of lanthanide and Y accumulation in the zone of hypergenesis. At the same time, published data on the REE and Y distribution in the weathering horizons are rather scant and contain sometimes contradictory information [6, 12, 14, 22, et al.]. Such contradictory data may be related to methodological problems that occur during the study of elements in the weathering processes. These have been partially already discussed in [8, 11].

Even when using the methods of absolute masses or control elements, not all weathering horizons are applicable for solving questions of element mobility in processes of surficial rock alterations. The uneven distribution of the basic minerals that carry specific elements in the substrate, lateral introduction of various components into the studied sections from topographically higher portions of weathering horizons, redistribution of matter between various horizons of a profile, and, especially, the superimposition of various epigenetic processes, the strongly alternating primary element distribution in the developing weathering horizon may all essentially lead to the use of current methods, that do not allow correct evaluation of element mobilization during the weathering stages. The pattern of element mobilization also emerges when using the absolute mass method, if the substrate is correlatable with those weathering horizon zones in which weathering products have been significantly accumulated and compacted. In such cases, great volume differences exist between the source rocks and the weathered rocks. Literature data on the distribution of various components in the weathering horizons, recalculated within certain limitations, are unavailable. Therefore, it is unclear to what degree the migration activity of elements during hypergenetic rock alteration could be determined in the studied profiles.

The study objectives, relating to the distribution of REE and Y during weathering in the present paper, took into account the above-stated limitations.

Objectives and Methods of Study. The behavior of REE and Y during hypergenetic alterations was studied in Mesozoic, Neogene, and Paleogene areas of clayey weathering horizons on Precambrian granites, gabbro-diorites, and pyroxenites in the same region of the Pre-Azovian Crystalline Shield. These horizons formed during the same climatic stage, within the same climatic zone. Therefore, it may be assumed that the basic parameters that influenced weathering on various source rocks were similar. The subject has earlier been treated in conjunction with study results from weathering horizons of numerous other elements [4, 5, et al.] and during mineralogical-petrological and geochemical study of the substrate [13]. Mostly, 20-kg composite samples were used. They were typical of the source rocks and a well-defined eluvial mantle zone. These samples were mixed from individual, 1.5-2.0-kg samples that reflected a sequence of gradually increasing hypergenetic changes in the substrate and

Institute of Mineralogy, Geochemistry, and Crystallochemistry of Rare Elements, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 12-26, May-June, 1986. Original article submitted January 23, 1985.

TABLE 1. Mineralogical Composition of Rocks in the Studied Weathering Interval, in Percentages

Rock	Massif	Zone	Specific gravity, g/cm ³	Quartz	Feldspar	Biotite	Muscovite	Pyroxene	Amphiboles	Clay	Accessory minerals	Accessory mineral carriers of rare earth elements and Y
Two-mica granite	Starodubovsk	G	2,37	36,4	61,7	0,5	0,5	—	—	—	0,9	Fluorite, cyrtolite, xenotime
		KG ₁	1,98	37,2	42,6	—	—	—	—	20,1	0,07	Cyrtolite, xenotime
Same	Ekaterinovsk	G	2,39	30,25	66,9	1,75	1,08	—	—	—	0,04	Monazite, cyrtolite, xenotime
		KZ	1,63	33,36	—	—	—	—	—	66,6	0,035	Rhabdophanite, cyrtolite
Biotite granite	Kal'mius-Elanchik	GD	2,36	25,5	69,7	2,9	—	—	0,43	—	1,74	Apatite, ilmenite, zircon
		VGD	1,67	30,8	—	—	—	—	—	68,1	1,1	Zircon and ilmenite
Gabbro-diorite	Ancient (Old) Crimean Region	GD	2,63	—	63	—	—	5	25	—	7	Apatite, magnetite
		VGD	1,82	—	65	—	—	—	15	15	5	Magnetite, apatite, limonite
Pyroxenite	Oktyabr'sk	pr	3,02	—	16,9	—	—	61,1	—	—	22	Magnetite, ilmenite
		GZ	1,43	—	0,04	—	—	0,63	2,1	73,7	22,9	Limonite, ilmenite, magnetite

Note: G) granite; KG) kaolinitized granites; KZ) kaolinitized zone; GD) gabbro-diorite; VGD) weathered gabbro-diorite; Pr) pyroxenite; GZ) clay zone.

TABLE 2. Element Distribution in the Weathered Rock Profiles

Rock	Massif	Zone	Specific gravity, g/cm ³	Σ REE	La	Ce	Nd	Sm	Eu	Yb	Lu	Y	F	Na	K	Fe
Granite	Starodubovsk	G	2,37	1086	242	482	223	95	1,43	37,6	5,0	590	12,4	66,6	77,3	28,2
		DZ	2,35	790	160	342	179	73	1,21	31,0	4,0	472	9,1	64,5	76,1	26,3
		KG ₁	2,15	420	83	193	88	37	0,78	16,6	1,9	312	3,4	49,0	71,7	19,5
		KG ₂	1,98	275	62	125	52	19	0,68	14,8	1,74	222	1,5	19,8	67,3	19,8
	Ekaterinovsk	K _s		0,25	0,25	0,26	0,23	0,20	0,47	0,39	0,35	0,37	0,12	0,30	0,87	0,70
		G	2,39	217	72	131	—	8,3	1,65	3,3	0,43	86	0,95	59,6	93,6	27,7
		KG	2,27	222	75	129	—	11,6	2,15	4,0	0,45	91	0,75	50,6	74,1	29,5
		KZ	1,63	175	62,5	97,3	—	9,1	1,66	3,5	0,44	72	0,32	1,3	22,2	17,6
	Kal'mius-Elanchik	K _s		0,80	0,87	0,74	—	1,09	1,0	1,06	1,02	0,83	0,33	0,02	0,24	0,63
		G	2,36	396	125	233	—	22	7,1	7,15	1,55	113	0,85	62,3	92,0	61,3
		KG	1,86	416	133	228	—	34	11,1	8,6	1,55	119	0,27	6,2	81,3	83,7
		KZ	1,67	401	130	235	—	24	7,5	3,7	0,68	26,7	0,17	1,0	7,8	28,4
	Ancient Old Cdmean Region	K _s		1,03	1,04	1,0	—	1,09	1,05	0,52	0,44	0,23	0,20	0,016	0,085	0,46
		GD	2,63	213	58	117	—	16,5	19,0	2,3	0,46	63,0	1,80	81,0	88,3	152
		DZ	2,43	171	47	91	—	11,7	18,4	2,3	0,41	58,3	1,20	64,7	83,1	148
		VGD	1,82	134	36	73	—	10,7	14,0	<1,8	<0,27	38,0	0,68	52,3	62,3	105
Gabbro-diorite	Oktyabr'sk	K _s		0,63	0,62	0,62	—	0,65	0,74	<0,78	<0,58	0,6	0,38	0,64	0,70	0,60
		PR	3,02	223	66	134	—	15	3,6	3,7	0,75	—	—	18,4	4,8	501
		GZ	1,43	111	34	66	—	7,6	1,9	1,6	0,31	—	—	2,9	1,5	214
		K _s		0,50	0,51	0,49	—	0,51	0,52	0,43	0,41	—	—	0,16	0,31	0,43

Note: DZ) disintegration zone; K) stability ratio. REE concentration in Y given in grams/cu m; for other elements: in kg/m³.

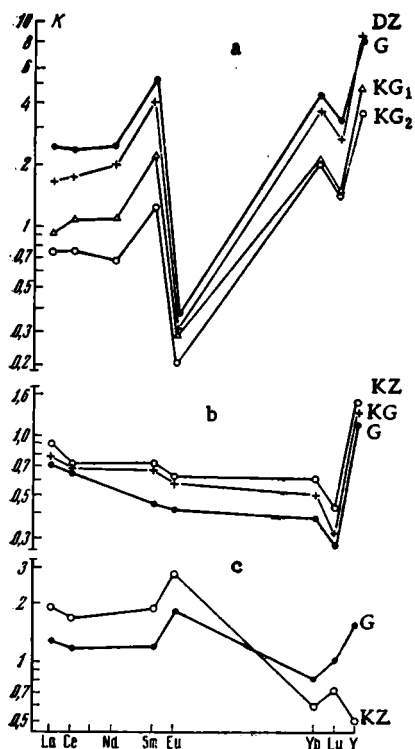


Fig. 1

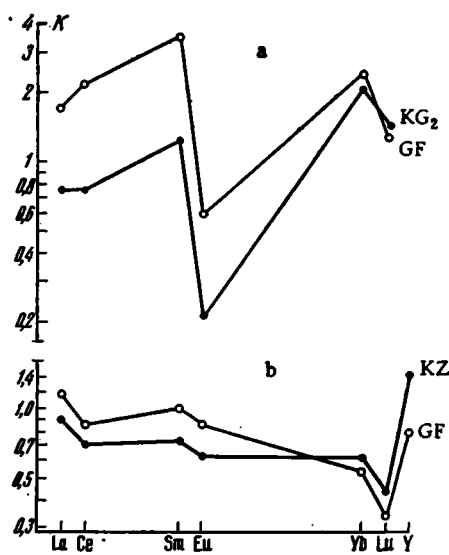


Fig. 2

Fig. 1. Evolution of the REE composition during granite weathering. a) Starodubovsk massif; b) Ekaterinovsk massif; c) Kal' mius-Elanchik massif. The REE element compositions in this figure and in Figs. 2-4 were fixed in relation to the average REE composition in clayey shales (crustal sedimentary rock) [20, 26]. Symbols, as shown in Figs. 2 and 3 and Tables 1-3.

Fig. 2. REE compositions in the samples of the weathering horizons and in kaolinite in three samples. a) Starodubovsk massif; b) Ekaterinovsk massif.

various horizons in the weathering profile, as well as source rocks. The specific samples were supplemented by others, from which petrographic thin sections were prepared. Clay fractions, isolated by the method of subcolloidal settling, have been isolated from the composite samples and their mineral and chemical compositions established.

Results of the complete quantitative mineralogical sample analysis by Danilova during the preliminary study of the profiles helped to evaluate the heterogeneity of minerals that were carriers of rare earth elements (REE) and Y in the source rocks. Along with the results of petrographic thin section analyses, they also provided the needed information on effects of superimposed epigenetic processes and the redistribution of matter within the weathering horizons. The significant contribution of the effects was shown by the petrographic and mineralogic aspects of rocks in various weathering zones. A complete silicate analysis and identification of several REE and of Y supplemented the work. These data, along with field information, allowed evaluation of the suitability of various sections for the study of REE and Y mobility during hypergenetic rock alteration processes. Five profiles were selected for the study of lanthanide and Y distribution (Table 1).

The REE distribution was determined by the neutron-activation method, Y, by x-ray spectrum analysis in the composite samples. The present authors conducted the analysis. In most samples, six lanthanides were determined: La and Ce of the light REE; Sm and Eu of the intermediate group, and Yb and Lu, representing heavy REE. The lanthanides geochemically are closely related to each other. For this reason, conclusions on the analyzed REE characterizes the behavior of the whole group reliably. All the analytical work has been performed in the laboratories of IMGRE.

TABLE 3. Changing Role of Individual La-Elements in Rare-Earth Element (REE) Composition during Rock Weathering.

Massif	Zone	Σ six REE, g/ton	% of total of six REE						La/Ce	La/Sm	La/Eu	La/Yb	Ce/Sm	Ce/Yb	Ce/Eu	Sm/Eu	Sm/Yb	Eu-Yb
			La	Ce	Sm	Eu	Yb	Lu										
Stanodubovsk	G	364	28,0	55,9	11,0	0,16	4,35	0,58	0,50	2,55	170	6,4	5,0	336	12,6	66,4	2,5	0,04
	DZ	260	26,2	55,9	11,9	0,20	5,07	0,65	0,47	2,19	136	5,2	4,7	292	11,2	60,3	2,4	0,04
	KG ₁	153	25,0	58,1	11,13	0,23	4,99	0,57	0,43	2,23	76	5,0	5,2	178	11,7	47,4	2,2	0,05
	KG ₂	113	27,8	56,0	8,5	0,30	6,63	0,78	0,49	3,29	91	4,1	6,7	185	8,4	27,9	1,2	0,05
	KG-GF	291	24,4	62,8	9,2	0,32	2,98	0,27	0,39	2,63	75	8,2	6,8	192	21,0	28,4	3,1	0,11
Ekaterinovsk	G	91	33,0	60,5	3,85	0,76	1,54	0,20	0,55	8,6	43,5	21,4	15,7	79,7	39,3	5,0	2,5	0,49
	KG	98	33,6	58,1	5,20	0,97	1,83	0,20	0,58	6,5	34,7	18,3	11,2	60,0	31,6	5,4	2,8	0,53
	KZ	107	35,7	55,9	5,17	0,94	2,02	0,27	0,64	6,9	37,6	17,8	10,8	58,6	27,8	5,4	2,6	0,47
	KZ-GF	131	36,7	54,7	5,90	1,07	1,45	0,16	0,67	6,2	34,3	25,2	9,3	51,1	37,6	5,5	4,0	0,74
Kal'mius-Elanchik	G	168	31,5	58,8	5,5	1,80	1,8	0,39	0,54	5,7	17,6	17,5	10,6	32,8	32,6	3,1	3,1	0,99
	KG	224	32,0	54,8	8,2	2,66	2,0	0,37	0,58	3,9	12,0	15,4	6,7	20,5	26,5	3,0	3,9	1,29
	KZ	240	32,4	58,6	6,0	1,87	0,92	0,17	0,55	5,4	17,3	35,1	9,8	31,3	63,5	3,2	6,5	2,02
Ancient Old Crimean Region	GD	81	27,2	55,0	7,7	8,9	1,07	0,21	0,49	3,5	3,0	25,2	7,1	6,1	50,8	0,87	7,2	8,2
	DZ	70	27,5	53,3	6,8	10,8	1,34	0,24	0,51	4,0	2,5	20,4	7,8	4,9	39,5	0,63	5,1	8,0
	VGD	~74	27,0	54,5	8,0	10,4	<1,34	<0,20	0,49	3,3	2,5	>20,0	6,8	5,2	>40,5	0,76	>5,9	>7,8
Oktyabr'sk	Pr	74	29,6	60,0	6,7	1,6	1,7	0,33	0,49	4,4	18,3	17,8	8,9	37,2	36,2	4,2	4,0	0,97
	GZ	78	30,5	59,3	6,8	1,7	1,4	0,28	0,51	4,5	17,9	21,2	8,7	34,7	41,2	4,0	4,7	1,20

Note: GF) clayey fraction.

The element mobility during hypergenetic rock alteration has been calculated by the absolute mass (isochoric) method through calculation of the stability coefficient (K_y) of elements, the ratio of the amount of elements in 1 m³ of the most weathered rock and their amount of 1 m³ of unweathered source rock.

Study Results. Change in the mineralogy of the source rock, due to weathering, is shown in Table 1.

REE and Y in Profiles of Weathered Granites. The stability ratio of the total REE showed a wide range between various profiles (0.25-1.00) (Table 2). Lanthanides displayed the greatest mobility in profiles where hypergenetic alteration processes in granites were less explicit than in some others (Table, 1, Starodubovsk massif). What is the reason for the different behavior of these elements? As shown before, it can safely be predicted that the basic parameters that govern granite weathering were quite similar. Therefore, the reason for sharp differences in lanthanide behavior may be related to the composition of the source rocks; to the REE-distribution in their minerals.

Starodubovsk Massif. The tentative calculation of the lanthanide and Y distribution in the albitized, rare metal element-bearing granites of this massif, with calculation of the most common REE and of Y in minerals of the granitoids [1, 9, 10, 15], has indicated that over 70% of the total REE and about 85% of Y concentrate in accessory minerals. Large portion of the total occurs in fluorite, the main accessory mineral in granites. Among rock-forming minerals, feldspars are the most important carriers of these elements. The most intensive hypergenetic alteration stage in rocks of this massif in the studied section was a 5-m zone of kaolinitized granites (KG₂) that consisted of 20% clay matter. The kaolin zone was eroded.

Results of the quantitative mineral analysis of samples from this profile have indicated that fluorite had decomposed slightly during weathering; it is practically absent in the kaolinitized granites (zone KG₂). Most importantly, during mineral disintegration, not only REE are freed, but also F. REE are associated strongly with newly forming hydroxides of low solubility. Complex, soluble compounds may form with lanthanides and Y, often in combination with CO₃²⁻ [7, 23]. The stability coefficient of F in the given profile of weathering was 0.12 (Table 2); this element therefore is an actively migrating component. F probably entrains not only the REE of fluorite, but also contributes to their leaching from other rock-forming and accessory minerals. As the result, the kaolinitized granites of the Starodubovsk Massif contain only 20% of the total REE, in comparison with the source rock content. Apparently, the close tie between lanthanides and fluorite is indicated by the higher mobility of REE in this weathering stage, in comparison with Na, K, and Fe (Table 2).

It is important to note the behavior during weathering of individual lanthanides and Y (Table 3, Fig. 1). Sm and Nd are expelled from the profile at the highest rates during weathering ($K_y = 0.2-0.23$), followed by La and Ce ($K_y = 0.25-0.26$). Thus, the light lanthanides and the particularly immediate ones are involved. The most passive element is Eu ($K_y = 0.46$), which is severely depleted in original REE content derived from the source granites in the Starodubovsk massif (Fig. 1). The depletion is obviously the result of the low Eu content in fluorite, the primary REE-carrier in these rocks. Quite unexpectedly, Eu is associated with heavy (Yb and Lu) lanthanides ($K_y = 0.35-0.39$) and also Y ($K_y = 0.37$). This explains the high degree of inertness of these elements, especially of the heavy lanthanides and Y. Due to chemical characteristics that may lead to the ability to form more stable complexes in many natural processes, these elements are more mobile during migration than the rest of the REE [1, 15]. One should turn to the peculiar distribution patterns of REE and Y in minerals of the source rocks. A significant portion of Yb, Lu and Y is associated with accessory minerals (xenotime and cyrtolite), that are relatively stable during weathering processes. This contrasts with the behavior of light and intermediate REEs in the Starodubovsk granites. The amount of these minerals in the weathering profile, in contrast with fluorite, changes only slightly with K_y values higher than that of heavy lanthanides and Y.

The highest K_y values of Eu in the weathering horizon may be explained by the fact that the bulk of the element — in contrast with other REE — apparently concentrated not in fluorite which was depleted in the element, but usually in feldspars [20]. Two-thirds of the feldspar volume in the source rocks was retained in the KG₂ zone (Table 1). This alone blocked the entry of Eu beyond the weathering horizon.

Thus, during hypergenetic alteration of the Starodubovsk granites, those rare-earth elements were the most active migrants (Sm, Nd, La, and Ce) that were most abundant in the fluor-

TABLE 4. Role of Clay in the Balance of REE and Y Distribution in Granite Weathering Horizons

Massif	Zone (amount of clay, in %)	Rock	Concn., g/ton						
			La	Ce	Sm	Eu	Yb	Lu	Y
Starodubovsk	KG ₂ (20,1)	I	31	63	9,4	0,34	7,5	0,88	—
		II	71	183	27,0	0,95	8,7	0,80	—
		r.c.	46	58	58	56	23	18	—
Ekaterinovsk	KZ (66,6)	I	38	59,5	5,5	1,02	2,15	0,27	44
		II	48	71,5	7,7	1,40	1,90	0,21	24
		r.c.	84	80	93	91	59	52	36

Note: r.c. — the role of clay (9) (the amount of an element associated with the clay fraction, expressed in % of its total content in the sample). I — total sample; II — clay fraction. Other symbols: as in Table 1.

ite of the source rocks. Fluorite disintegrates quickly and introduces F into the solution. The chemical characteristics of individual lanthanide elements that influenced in a certain way their degree of mobility, were overwhelmed by more important factors that determined the REE distribution.

Ekaterinovsk and Kal'mius-Elanchik Massifs. In contrast with the Starodubovsk granites, the REE and Y distribution in the two other massifs is significantly different. Most (70-80%) of the lanthanides and Y occur in rock-forming minerals, mostly in feldspars. Accessory minerals contain large portions of REE and Y in rocks of the Ekaterinovsk massif. Fluorite occurs only as scattered grains in the granites.

Maximum hypergenetic rock alteration in these two massifs created 15-25-m-thick kaolinized zones. All feldspars and micas in these zones were replaced by kaolinite. The kaolinite content reached 68% (Table 1).

The absence of F in the solutions that circulated in the weathering profiles in these two massifs influenced the sharp drop in the gross mobility of REE ($K_y = 0.8-1.0$; Table 2). The slowest migration rates occurred in the intermediate lanthanides (Sm and Eu). They stayed within the weathering horizon. In the weathering horizon of the Ekaterinovsk massif, heavy lanthanides (Yb and Lu) occur. Apparently, the mobility of these elements and Y is mostly determined by the relatively stable accessory minerals cyrtolite and xenotime that carry the elements in the source rocks. In comparison with the granite source rock, their quantity did not change much. The light lanthanides (La and Ce) were the most mobile in the Ekaterinovsk massif weathering horizon; 13-26% of their initial total had been lost from the weathering profile (Table 2).

The above listed rare metal-bearing accessory minerals are absent from granites of the Kal'mius-Elanchik massif. Heavy lanthanides greatly predominate here, just as light and intermediate lanthanides, that occur in the rock-forming minerals. Thus, heavy, intermediate, and light lanthanides were present under about identical conditions in the weathering profile as weathering agents attacked them. This probably did not decisively influence the fact that heavy REE due to their chemical characteristics, behaved as more actively migrating elements. About half of their initial amount in the source rocks left the weathering horizon ($K_y = 0.44-0.52$). They have included Y which was even more mobile ($K_y = 0.23$). At the same time, the light lanthanides (La and Ce) are similarly of intermediate character and are inert in this weathering profile. Within the accuracy range of analytical methods, their K_y value approximately equals unity (Table 2).

In the kaolinitized granite zone of the Ekaterinovsk and Kal'mius-Elanchik massifs where the rocks contain significant amounts of iron, the total amounts of most of the REEs and Y, also of Fe, have increased in comparison with the source rocks (Table 2). This is most notable in intermediate lanthanides Sm and Eu, expressed in their changed ratios in the total REE, and correspondingly, in the changed ratio values to other REE (Table 3, Fig. 1). At the same time, the amount of Ce does not increase and the amount of La remains practically the same (Table 2). Apparently, the increase in the absolute quantities of the total REE and Y is controlled by the Fe hydroxides that absorb these elements from solutions [1]. Addition-

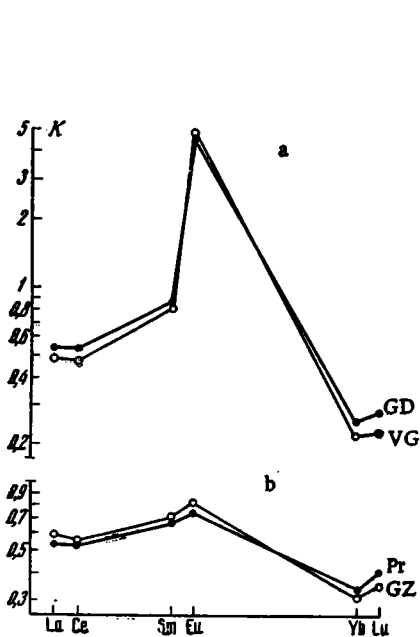


Fig. 3

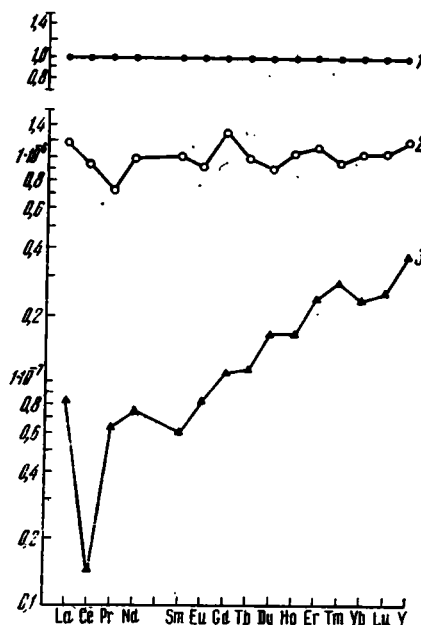


Fig. 4

Fig. 3. Evolution of the REE composition during melanocratic rock weathering. a) Gabbro-diorite; b) pyroxenite.

Fig. 4. REE compositions in river [27] and ocean [29] water. 1) Clay shales (sedimentary rocks); 2) river waters; 3) ocean waters.

al amounts of Fe, REE, and Y may come from the upper parts of the developing profiles, from the modern kaolin zone and through lateral addition from topographically higher weathering horizons of granite massifs in the immediate vicinity. The zone of iron-enriched kaolinized granites may be thought of as an intermediate, temporary accumulation stage of these elements during weathering, although epigenetic effects may have also been superimposed.

REE and Y in the Clay Fraction of the Weathering Horizons of Granites. In comparing the analysis results of average samples, taken in the weathering horizons of granites in the Starodubrovsk and Ekaterinovsk massifs and of kaolinite, isolated from these samples (Table 4, Fig. 2), it was established that most REEs have a higher concentration in the kaolinite than in the average sample. An exception is Lu in the weathering horizon of the Starodubrovsk massif and Lu, Yb (heavy lanthanides), and Y in the weathering profile of the Ekaterinovsk massif. Their peculiar distribution pattern in these profiles may be explained not only by the lesser absorption of heavy REEs and Y by clay matter that may be assumed on the basis of data on their chemical characteristic [21]. In addition, significant amounts of these elements are tied to accessory minerals that, as shown earlier, were relatively stable during the weathering process. This is in agreement with data on the role of clay in the REE and Y distribution in kaolinitized granites and in the kaolin zone of these granite massifs. Clay plays the least role with respect to heavy lanthanides and Y and the greatest with respect to intermediate and also light REE (Table 4).

In comparison with the lanthanide composition, as established from sample data in the weathering horizon, in general, and also for source granites in the kaolinite of the Starodubrovsk massif, the role of Ce and intermediate REE increases at the expense of La and heavy lanthanides (Table 3, Figs. 1 and 2). The REE content in the weathering horizon kaolinite fraction of the Ekaterinovsk massif, in comparison with the same standards, has also been depleted in heavy lanthanides and Y, and enriched in intermediate REEs. But, in contrast with kaolinite of the Starodubrovsk massif, the amount of Ce decreased and that of La increased in the kaolinite (Table 3, Figs. 1 and 2). Despite such changes in the REE compositions of the clay fractions, the most typical characteristics of lanthanide composition in the weathering horizons, as those of the granite source rocks, have been inherited by the clays (Table 3, Figs. 1 and 2). The concentration level of total REE in the substrate rocks has also been inherited and this confirms the trends already noted in [6, 12, 14, 15]. Consequently, the total amounts of REE, absorbed by clays, are essentially determined by their concentrations in the medium in which clays form.

Thus, the distribution characteristics of lanthanides and Y in rock-forming and accessory minerals, the different stability of these minerals with respect to weathering agents, the particular chemical composition of the solutions that form in the weathering horizons, the specifics of the chemical characteristics of REE adequately clarify both the total mobility of the REE group and the quite complex, ambiguous behavior of individual lanthanides and Y during the process of hypergenetic alteration of these rocks. When the granite source rocks are enriched in fluorite in which the overwhelming portion of the REE and Y of the substrate had concentrated, all lanthanides and Y are very mobile in the weathering horizon. However, fluorite-enrichment is more an anomaly than the norm. Among the studied rocks, granites of the Kal'mius-Elanchik massif are closest in composition to standard granites. If one accepts the REE distribution in the weathering horizon of these rocks as a basis and supplements it with the data from other profiles, this leads to a trend of a quite inert behavior of the total REE during the process of hypergenetic change of granitoids during greater mobilization of Y and of the heavy lanthanides. It causes the passive behavior of intermediate lanthanides and intermediate behavior of the light lanthanides.

REE in Weathering Profiles of Gabbro-Diorites and Pyroxenites. A tentative calculation of the REE and Y concentrations in minerals that contain them in gabbro-diorites and pyroxenites has been performed in the same way as done for the granites. In these rocks, 75% of the total REE and Y content occurs in the rock-forming minerals, similarly as in granites of the Kal'mius-Elanchik and Ekaterinovsk massifs. Among the rock-forming minerals in the gabbro-diorites feldspar (38%) and amphiboles (30%) contain most of the lanthanides; among the accessory minerals, apatite (18%). Of the total REE content in pyroxenites, 70% occurs in pyroxenes and about 15% in magnetite.

The peak stage of hypergenetic alterations in the weathering horizon of gabbro-diorites is represented by a ~1-m-thick weathering zone that contains maximum 15% of clayey matter, composed of chlorite, sericite, and clay. A clay zone is absent. In the upper part of the weathering zone of pyroxenities, a 2-m-thick clayey zone includes 74% of nontronite, chlorite, palygorskite aggregate (Table 1).

The mobility of the total REE in the weathering horizons of gabbro-diorites ($K_y = 0.63$) and pyroxenites ($K_y = 0.5$) has been greater than in the weathering horizon of granites in the Kal'mius-Elanchik and Ekaterinovsk massifs ($K_y = 0.8-1$; Table 2). The high mobility of the total REE in the weathering horizons of melanocratic rocks, in contrast with that of granites, is explainable by the more intensive loss of La and Ce from the first light lanthanides that control the amount of the total REE in the gabbro-diorites, pyroxenites, and granites. The lesser stability of light lanthanides in the weathering horizons of melanocratic rocks, in contrast with those of granites, is hard to explain. In both cases, the dominant amounts of these elements are found in rock-forming minerals that are completely transformed into clays in weathering profiles of pyroxenites and granites of the Kal'mius-Elanchik massifs. There is no reason to assume that kaolinite in the weathering horizons of granites had a greater absorption capacity with respect to these elements than chlorite-sericite-clay minerals had in weathering profiles of gabbro-diorite rocks, or a higher capacity than found in nontronite-chlorite-palygorskite aggregates in pyroxenite weathering horizons. The latter weathering horizons contain significant amounts of Fe and Mn hydroxides that may actively absorb REE. It is possible that in the weathering horizons of melanocratic rocks, conditions for the formation of soluble REE compounds are more favorable and the factors that make these conditions may include variations in weathering conditions or the chemical composition of the rocks.

Analysis of changes in the REE composition during weathering of melanocratic rocks has shown less contrast than found in granites. A slight tendency toward a more intensive loss of Y and of heavy lanthanides was nevertheless established (Tables 2 and 3, and Fig. 3). These elements are characterized by minimum K_y values among the REE. The most stable were the K_y values of intermediate REE in weathering horizons of gabbro-diorites and granites. Values of light lanthanides occupied average positions. In the weathering horizons of pyroxenites, the intermediate and light REE showed no differences in their degree of mobility (Table 2). These facts are reflected in the changed ratios of individual lanthanides in the composition of rare-earth elements and in their mutual ratios (Table 3). Despite these alterations and those that took place in the weathering horizons of granites, all basic characteristics of the REE composition in the gabbro-diorite and pyroxenite source rocks can be traced through their weathering products (Fig. 3).

TABLE 5. Median Values of REE in the Ocean ($n \cdot 10^{-8}$ g/ton), in the Crust (g/ton) and Their Coefficients of "Marine-Affinity" (MA).

Category	Σ total REE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Ocean water	1260	340	120	64	280	45	13	70	14	91	22	87	17	82	15	1300
Earth's crust	89,3	16	31	4,5	17	4,2	1,3	4,2	0,7	3,85	0,9	2,6	0,4	2,3	0,34	23
KT $\cdot 10^8$	14,1	21,2	3,9	14,2	16,5	10,7	10,0	16,6	20,0	23,6	24,4	33,5	42,5	35,6	44,1	57,0

Discussion of Results. The Mobility of REE and Y in the Initial Rock Weathering Stage.

In the studied clayey weathering horizons, the lanthanides and Y behave as very inert elements and active migrants. When they actively leave the weathering horizon, the dynamics of their loss depends largely on the stage in which most of the main minerals that carry REE and Y begin their disintegration process. If the dominant majority of the lanthanides and Y occur in rock-forming minerals, it cannot be expected that their significant portion, presented in the source rocks, would have been lost from the zone of disintegration during the initial stage of hypergenetic alteration. The rock-forming minerals in this zone are basically still fresh and have not disintegrated. Only 7% Y and 20% of the total REE was lost from the initial amount in the substrate in the disintegration zone of gabbro-diorites (75% of the total REE and Y was tied to rock-forming minerals). A certain portion of the lanthanide loss apparently occurred as the result of partial dissolution of the accessory apatite which contained ~18% of the total REE of the source rock.

If the bulk of the total REE and Y occur not in rock-forming minerals but in stable accessory minerals, resistant to weathering, then the mobility of these elements during the formation stage of the zone of disintegration obviously may be even lower. On the contrary, accessory minerals that disintegrate faster during weathering in comparison with rock-forming minerals, may have an important impact on the lanthanide and Y mobility in the initial stage of hypergenetic rock alteration if the bulk of these elements occurs in these minerals. Thus, in the disintegration zone of Starodubovsk massif granites, enriched in fluorite, REE and Y are lost with greater intensity than from the disintegration zone of gabbro-diorites. Even under such favorable conditions, the Y loss does not exceed 20% and the total REE loss remains less than 27% of their original amount in the source rocks.

Fractionation of REE in the Weathering Process. In the studied profiles of leuco- and melanocratic rocks, a slight tendency exists for a more intensive Y and heavy lanthanide loss; also, partially for the loss of light rare-earth elements. As the result, in the weathering products a slight enrichment takes place in the intermediate lanthanides of the REE, in comparison with the REE content of the source rocks. Weathering thus increases the ratio of intermediate lanthanides. However, despite the changed role of individual lanthanides in the total REE during hypergenetic rock alteration, the basic REE composition characteristics of the substrate are reflected in the weathering products. Thus, even when 50-75% of the total REE is lost from the weathering profile, the weathering products, including clays, retained all main features of the lanthanide composition in the source substrate. Such indications of the source rocks are preserved, as shown in Figs. 1-3. In most instances, the weathering products also reflect REE and Y concentrations in the source rocks (Tables 2 and 4). These data and those in [6, 12, 14 15] provide the best foundations for using REE data in solving problems of sediment genesis in depositional basins and in exploration geochemistry.

Accumulation of REE and Y in Weathering Horizons. Our results (Table 2) indicate that, at least in certain instances, REE and Y occur as very inert migrants in the weathering profiles. Under such conditions, the intensity of loss of highly mobile rock-forming components and the corresponding intensity in the decrease of the total volume of weathered rocks may speed the removal of lanthanides and Y from the weathering horizon. As the result, due to passive accumulation, the concentration of REE and Y, defined not in absolute values (g/m^3) but in weight percentages or in grams per ton, may increase in comparison with the substrate concentration. The relative REE concentration in the clay zone of the Kal'mius-Elanchik massif is greater than 30% (Table 3), corresponding to the change in the volumetric weight of the rock in this zone, in comparison with that of the substrate. Thus, the lanthanide

loss from the weathering profile is practically nil, when its total value (Σ REE) is considered. Passive accumulation of the total REE in the weathering horizons usually occurs by means of light and intermediate lanthanides that determine the total concentration of REE also in the source rocks. Increase in the concentration of heavy lanthanides and Y occurs less frequently due to their high mobility. It takes place by relative accumulation of stable accessory minerals that include these elements in the weathering horizon.

Accumulation of REE and Y during the chemical rock disintegration process may be traced to the final stages — the formation of laterite. Usually it is related, as in the clayey weathering horizons, to more intensive loss of rock-forming components. To a lesser extent, active concentration also occurs through redistribution of lanthanides between portions of the weathering horizon. Data in the literature indicate that the Y and REE concentration values usually are low in the laterites: 0.00n and 0.0n g/ton, respectively [16, 18]. The maximum concentrations occur in those instances when relict rare metal-bearing accessory minerals or hypergenetic recrystallization products of these minerals are preserved in the laterites in larger quantities. Such laterites formed on rocks that were enriched in these minerals [24, 28, etc.]. However, the lanthanide and Y concentrating process, through reworking of clayey weathering horizons, is more effective. This was the process by which the commercial REE and Y concentrations formed in monazite-xenotime-cyrtolite placers [17].

Migration Activity of REE and Y in the Weathering Cycle. Estimation of the mobility of the total REE, and also of the degree of the mobility of individual lanthanides and Y during various rock weathering stages and on the whole, in the zone of hypergenesis in weathering profiles of rocks encounters great difficulties. The mobility of the total REE, individual lanthanides and Y differs greatly from profile to profile. For well-founded estimations, further data are needed from appropriate weathering profiles. More objective data on the mobility of REE and Y in the weathering cycle and from a broader area in the zone of hypergenesis may be attained by evaluating the results of the hypergenetic rock alteration process by determining of their average coefficient of migration in water (ACMW): the ratio of the average concentration of the element in soluble form in river waters and its average concentration in the earth's crust [3]. However, few reliable analyses exist on the concentrations of REE and Y in soluble form in river waters. Only analyses of two rivers, the Garonne and the Dordogne, are available [27]. At best, these reflect only the levels of the total REE and Y concentrations but not the average REE concentration of river waters on earth. These values are very low ($2 \cdot 10^{-4}$ g/ton for total REE and $0.43 \cdot 10^{-4}$ for Y). The ACMW values of lanthanides and Y, calculated according to these data, are very low: $(1-2) \cdot 10^{-6}$. Earlier, one author grouped lanthanides with the passive migrants in water [19]. He based this on preliminary data on the concentration of the total REE in river water. Analyses of river waters in France indicate their even lower migration activity in water.

These data contradict the significant mobility of REE and Y, shown in a number of instances in weathering profiles of water. As shown [4, 5, 25], the pattern indicates that the degree of element mobility in the hypergenetic zone defines their migrational routes in the weathering processes. Thus, the element mobility in profiles of recent and ancient weathering corresponds to the migration activity of the elements in water, as defined by the dimension of ACMW and the coefficient of thalassophilia (KT). This is the ratio between the average concentration of a given element dissolved in ocean water and its average value in the crust of the earth [2]. The calculated KT values (Table 5) of individual lanthanides characterize them as very passive migrants in water. They avoid the hydrosphere. The REE behave similarly to other hydrolyzers (Al, Ti, Sc, etc.). This corresponds with calculated values of their mobility in the zone of hypergenesis based on the dimension of ACMW and corresponds also with the degree of thalassophilia (marine affinity) of the total REE, as given earlier [2].

Thus, data on the lanthanide and Y migration in water somewhat contradicts conclusions on their high mobility in weathering profiles. However, no sufficient data yet exist to conclude that REE and Y are exceptions to the general rule. It is expected that further studies will determine that segment in the initial migration route of the REE where their most intensive conversion to the solid phase takes place, depleting the salt component of natural waters. Possibly, this segment includes both the weathering horizons and their immediately adjacent zones.

The coincidence of certain vital values, of lanthanide fractionation in the weathering horizons with the sequence of $Y > Lu > Tm > Yb > Er > Ho > Dy > La > Gd > Nd > Pr > Sm > Eu >$

Ce, where REE and Y are arranged in decreasing order of their thalassophilia, the following conclusions may be made:

(1) Y and also the heavy lanthanides (Yb and Lu) that exhibited a tendency toward a greater mobility in the weathering horizons, have maximum KT values and occur at the beginning of the sequence;

(2) Sm and Eu, the most inert in the weathering horizons have low KT values and occur at the end of the sequence;

(3) La occupies an intermediate position both in the weathering processes and in the migration activity sequence in water.

Only Ce displayed no specific behavior. Data in Table 5 show that this element has the lowest KT value among the REE. This value differs sharply from those of its neighboring lanthanides in terms of the numerical order. In the weathering profiles that we have studied, it does not distinguish itself by a peculiar degree of inertness, in comparison with other REE. Although data on river waters, as shown before, are not reliable, their use in tentative calculations may indicate that the role of Ce (as in the case of other lanthanides) in the composition of REE that are soluble in river waters, has not changed particularly in comparison with the average composition of lanthanides in the sedimentary rocks of the earth's crust (Fig. 4). The unique behavior of Ce, in contrast with other REE, probably occurs not so much on the continents as in the oceans.

Evidently, this is explainable by the peculiar chemical characteristics of the element, shown by the ability to oxidize to Ce^{4+} under conditions that occur in the zone of hypergenesis. This separates Ce from the other lanthanides [21]. In marine and oceanic waters, in contrast with continents, oxidation may occur easier. These waters represent a stable, low alkalinity, oxidizing medium that favor such a process [21]. The tetravalent Ce is distinguished by its greater ability for hydrolysis and, at the same time, for formation of chemical complexes [7]. This indicates that Ce may behave both very passively and also as a very active migrant element in water. In sulfate-chlorine systems of oceanic waters, the competing process of complex-formation is best expressed in carbonate waters [7]. Apparently, it is caused almost completely by the dominant process of hydrolysis that sharply lowers the migration ability of Ce^{4+} and allows its absorption by disperse systems to a greater extent than it happens with other REEs. This sorptional feature is the main factor in the removal of Ce and other rare elements and lanthanides from marine and oceanic waters and, in general, from natural waters [3].

The described behavior of Ce is only a hypothetical scheme. Further studies, related to the analysis of the composition of dissolved REE in river waters, may reveal that the depletion of natural waters in Ce represent an evolutionary phase that is initiated on the continents, including the weathering horizons. Thus, in determining the actual position of REE and Y in the migratory activity sequence of elements in the zone of hypergenesis, additional information is required on their distribution in the weathering processes and in the natural waters.

LITERATURE CITED

1. Yu. A. Balashov, Geochemistry of Rare Earth Elements [in Russian], Nauka, Moscow (1976).
2. T. F. Boiko, "Distribution of trace and certain halophilic elements in waters of terminal depositional basins," *Litol. Polezn. Iskop.*, No. 6, 152-157 (1968).
3. T. F. Boiko, Metal Content of Surface Waters and Brines [in Russian], Nauka, Moscow (1969).
4. T. F. Boiko, "Trace elements in the weathering horizons of gneisses in the Pre-Azov area," *Dokl. Akad. Nauk SSSR*, 186, No. 4, 936-939 (1969).
5. T. F. Boiko, Trace Elements in Salt Formations [in Russian], Nauka, Moscow (1973).
6. V. V. Burkov and E. K. Podporina, "Rare earth elements in weathering horizons of granitoids," *Dokl. Akad. Nauk SSSR*, 177, No. 3, 691-694 (1967).
7. S. R. Krainov, Geochemistry of Rare Elements in Ground Waters [in Russian], Nedra, Moscow (1973).
8. N. A. Lisitsyna, "Geochemical study methods of the weathering horizon," *Litol. Polezn. Iskop.*, No. 1, 3-18 (1966).
9. V. V. Lyakhovich, Trace Elements in Rock-Forming Minerals of Granitoids [in Russian], Nauka, Moscow (1972).

10. V. V. Lyakhovich, Trace Elements in Accessory Minerals of Granitoids [in Russian], Nauka, Moscow (1973).
11. A. I. Perel'man and S. G. Batulin, "Migrational sequence of elements in the weathering horizon," in: Weathering Horizons [in Russian], 4th edn., Izd. Akad. Nauk SSSR (1962).
12. E. K. Podporina and V. V. Burkov, "Rare-earth elements in the weathering process of biotite pyroxenites," *Litol. Polezn. Iskop.*, No. 4, 39-53 (1977).
13. K. I. Rozanov and D. A. Mineev, "Geochemical characteristics of Precambrian granitoids of the Pre-Azov area," *Geokhimiya*, No. 2, 238-250 (1973).
14. A. B. Ronov, Yu. A. Balashov, and A. A. Migdisov, "Geochemistry of rare-earth elements in the sedimentary cycle," *Geokhimiya*, No. 1, 3-19 (1967).
15. E. I. Semenov, "Yttrium, lanthanides," in: Geochemistry, Mineralogy and Genetic Types of Rare Element Deposits [in Russian], Vol. 1, Nauka, Moscow (1964), pp. 193-283.
16. V. A. Tenyakov, "Geochemistry of bauxites of basic genetic classes, formed within the main geotectonic structures of the earth's crust," in: Geochemistry of Platform and Geosynclinal Sedimentary Rocks and Ores of Phanerozoic and Upper Proterozoic Age [in Russian], GEOKhI, Moscow (1966), pp. 227-230.
17. N. P. Kheraskov, K. V. Potemkin, and A. I. Spitsyn, "Placer deposits of rare elements," in: Geochemistry, Mineralogy and Genetic Types of Rare Element Deposits [in Russian], Vol. 3, Nauka, Moscow (1966), pp. 634-651.
18. V. N. Kholodov and A. S. Koryakin, "Rare elements in bauxite deposits," in: Geochemistry, Mineralogy and Genetic Types of Rare Element Deposits [in Russian], Vol. 3, Nauka, Moscow (1966), pp. 652-668.
19. V. N. Kholodov, Yu. E. Baranov, T. F. Boiko, et al., "Genetic types of sedimentary deposits of rare elements and climatic zonation," in: Geochemistry of Sedimentary Rocks and Ores [in Russian], Nauka, Moscow (1968), pp. 308-324.
20. L. A. Haskin, F. A. Frei, R. A. Schmidt, and R. E. Smith, Distribution of Rare Elements in the Lithosphere and Cosmos [Russian translation], Mir, Moscow (1968).
21. V. V. Shcherbina, "Geochemical foundations of the distribution of rare elements," in: Geology of Rare Element Deposits [in Russian], 3rd edn., Gosgeoltekhizdat, Moscow (1959), pp. 44-59.
22. M. G. Edlin and V. A. Tenyakov, "Yttrium geochemistry in bauxites," in: Bauxites [in Russian], VIMS, Moscow (1980), pp. 192-199.
23. K. B. Yatsimirskii, I. A. Kostromina, Z. A. Sheka, et al., Chemistry of Complex Compounds of Rare Earth Elements [in Russian], Naukova Dumka, Kiev (1966).
24. J. Bodenhausen, "The mineral assemblage of some residual monazite and xenotime-rich cassiterite deposits of Banka (Indonesia), *Proc. Kon. Nederl. Akad. van wetenschappen*, Ser. B, 57, No. 3, 322-328 (1954).
25. T. F. Boiko, "Distribution of rare elements in the profiles of rock weathering and their migration activity in surface waters," *Proc. 2nd Intl. Symposium of Water-Rock Interaction*, Sec. 1, Inst. Geol., Strasbourg (1977), pp. 219-227.
26. M. A. Haskin and L. A. Haskin, "Rare earths in European shales: a redetermination," *Science*, 154, 507-509 (1966).
27. J. M. Martin, O. T. Hogdahl, and J. C. Phillipot, "Rare-earth element supply to the ocean," *J. Geophys. Res.*, 81, No. 18, 3117-3124 (1976).
28. W. C. Overstreet, "The geologic occurrence of monazite," U.S. Geol. Survey Prof. Paper No. 530 (1967).
29. K. K. Turekian, "Oceans, streams and atmosphere," in: Handbook of Geochemistry, K. Wedepohl (ed.), Springer-Verlag, Berlin (1969), pp. 297-323.

MINERAL COMPOSITION OF UPPER VISEAN DEPOSITS OF THE NORTHERN
DNIEPER-DONETS BASIN

E. Z. Ivanova

UDC 549:551.735(477.6)

The paper examines the mineral composition of Carboniferous sandstones and siltstones of the Dnieper-Donets Basin. It is shown that lands in Belorussia and within the Voronezh Massif were the source areas in Carboniferous time.

The mineral composition of Upper Visean sandstones and siltstones of the Dnieper-Donets Basin and, in particular, of its north margin has received little attention. The data available for the Dnieper-Donets Basin and the Donbass are presented in [1, 2, 4].

Many of the mineralogical (immersion) studies of Upper Visean clastic rocks carried out by the author for purposes of paleogeographic reconstruction are based on a large amount of drilling for oil and gas conducted in recent years by the production associations Chernigov-neftegazgeologiya and Poltavaneftegazgeologiya at the north margin of the Dnieper-Donets Basin.

The area of study covers a wide expanse stretching from the Bakhmach structure in the northwest to the Pionerskaya structure in the southeast.

The section of Upper Visean deposits of the region is composed of alternating clay rocks, sandstones, and siltstones interlayered with limestones. Argillites are predominant; sandy horizons and lenses make up between 20-50% of the thickness of the section, amounting to 20-60 m. The total thickness of the Upper Visean deposits varies between wide limits from the margin of the basin toward its submergence. For example, in the Turutinskaya area it is 154 m, in the Artyukhovskaya area it is 450 m, and in the Voloshkovskaya area it reaches 600 m.

A study of the mineral composition of Upper Visean clastic rocks of the region suggests that both the allogenic and the heavy mineral assemblages are represented by varieties resistant to weathering and transportation. Quartz is dominant among the light minerals; fragments of siliceous rocks, quartzites, granites, biotite, and muscovite are present; feldspars occur in small amounts. However, there are individual horizons of clastic rocks enriched in feldspars and fragments of granites, granite porphyries, extrusive rocks, etc.

Light Minerals. Quartz is the principal constituent of sandstones and siltstones, comprising 80-95% detrital material. Quartz grains in the vast majority of cases are angular to rounded or rounded, colorless, commonly with liquid, gas, and mineral inclusions. The surface textures of the grain are rough, uneven, and smooth, commonly with conchoidal fractures, overgrowths, and completely reconstructed crystals. In the area under study, grains with undulatory extinction (70-80%) and individual grains (at times as much as 10%) are dominant in the quartz.

Feldspar is a common rock-forming mineral, comprising 3-6% detrital material; in individual horizons the amount of feldspar increases to 50%. In the larger part of the section microcline is dominant; plagioclase occurs less commonly; however, in horizons where the feldspar content is high, a large amount of plagioclase is present. The feldspar grains are severely weathered, semirounded and unrounded.

The authigenic light mineral assemblage is represented by carbonates, kaolinite, quartz, etc.

Heavy Minerals. The occurrence and abundance of this group of minerals are presented in Table 1.

Chernigov Branch, Ukrainian Scientific-Research Institute of Geological Exploration, Chernigov, Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 27-31, May-June, 1986. Original article submitted July 7, 1984.



Fig. 1. A terrigenous mineralogical zonation of Upper Visean deposits at the north margin of the Dnieper-Donets Basin: 1) boundary faults; 2) boundaries of the basin center; 3) boundaries of the subprovinces; 4) structure; I-III) subprovinces (I - rutile-almandine-tourmaline-zircon; II - pyrope-jaspilite-rutile-tourmaline-zircon; III - rutile-tourmaline-zircon).

TABLE 1. Heavy Mineral Distribution in Upper Visean Deposits of the Northern Dnieper-Donets Basin

Mineral	Mineral content, %	Region		
		northwestern	southeastern	southern
Detrital or allogenic minerals				
Zircon	12-63	+	+	+
Garnets:				
almandine	2-25	+	-	-
pyrope	1-3	-	+	-
Tourmaline				
schorlite	3-18	+	-	+
elbaite	1-2	+	+	-
chromium-rich	4-11	+	+	+
Rutile	2-7	+	+	+
Sphene	1-3	+	+	+
Leucoxene	10-45	+	+	+
Hornblende	Individual grains	+	-	-
Kyanite (or disthene)	Same	+	+	-
Staurolite	"	+	+	-
Authigenic minerals				
Anatase	2-11	-	+	+
Brookite	4-57	+	+	+
Barite	1-5	+	+	+
Siderite	2-75	+	+	+
Pyrite	3-80	+	+	+

Note. "+" denotes the presence of a mineral, "-" denotes the absence of a mineral.

Zircon is the most ubiquitous heavy mineral. The grain color of zircons ranges from colorless through pink, brown, and yellow; some grains are color zoned. It occurs as well-edged, short columnar or long prismatic crystals with bipyramidal terminations and as well-rounded and angular grains. Zircon crystals are concentrated more commonly in the fine-grained fraction.

Garnets are represented by two varieties - pink and colorless almandines and red pyrope. The grains are isometric, rounded and angular with a semiconchoidal fracture. The surface textures of the grains are commonly finely imbricated. The highest concentrations and the coarsest grains (0.2-0.3 mm) are characteristic of the lower part of the Upper Visean.

Tourmaline occurs in the form of several varieties - brownish black, yellowish brown, and blue schorlite; pink and blue elbaite; colorless and brown dravite; and as green chromium-

rich crystals. The shape of the tourmaline grains is predominantly prismatic, rarely with pyramidal terminations, which is characteristic of rocks of finer grain size; in the sand fractions the crystal forms are more commonly semirounded prisms with truncated ends. A large number of the grains is well-rounded. The largest amount of tourmaline are found in the northwestern and southeastern parts of the region; average and minimal amounts are characteristic of the southern part.

Rutile is a persistent heavy mineral but is more commonly found in the upper part of the section. It is present in the form of elongated, ellipsoidal, rounded, and semirounded grains, irregular-shaped fragments and elongated prismatic crystals, occasionally with bi-pyramidal terminations. The color of the grains is red-brown and amber yellow.

Sphene is present in small amounts in the form of semirounded grains, commonly brownish.

Leucoxene in most cases is represented by rounded opaque grains, white and yellowish in reflected light.

Monazite, xenotime, orthite, and kyanite (disthene) are also found in small amounts.

Individual grains of hornblende and epidote are found in sandy horizons containing an elevated amount of feldspar. An occasional presence of heavy minerals resistant to weathering and transportation was noted in the Donbass [1].

Fragments of ferruginous quartzites (1-3%) are typical detrital components in the southeastern part.

The authigenic heavy mineral assemblages are represented by anatase, brookite, barite, celestite, and ferruginous carbonates.

The above data on the mineralogy of Upper Visean clastic rocks at the north margin of the basin permit conclusions to be drawn concerning the source areas of detrital material and the modes of its transport.

It should be pointed out that the total percentage by weight of the heavy fraction varies between wide limits — from 0.2 to 3%. In addition, it is nonuniform even within the same stratum. The highest concentrations of heavy minerals are characteristic of the fine-grained, well-sorted sandstones that formed under prolonged stable conditions. These sandstones have the distinctive characteristics of shallow marine deposits.

On the basis of the light fraction mineralogy of the Upper Visean siltstones and sandstones, the entire region of the Dnieper-Donets Basin should be characterized as a quartz supraprovince [3]. The studied composition and areal distribution of the heavy minerals have enabled a rutile-tourmaline-zircon terrigenous mineralogical province to be defined within the Upper Visean at the north margin of the basin and at the basin center. Detailed investigations have shown that there are differences in the mineral composition within this province, which have allowed three subprovinces to be identified: I — a rutile-almandine-tourmaline-zircon subprovince in the northwestern part of the marginal zone; II — a pyrope-jaspilite-rutile-tourmaline-zircon subprovince in the southeastern part of the marginal zone; and III — a rutile-tourmaline-zircon subprovince in the southern, submerged part of the region (see Fig. 1).

The above data suggest that the detrital components are represented by minerals exceedingly resistant to weathering and transporting agents, whose assemblage characterizes multiply redeposited sediments. The marked predominance of quartz among the light minerals and of zircon, tourmaline, rutile, and garnet among the heavy minerals indicates disintegration of old clastic sedimentary rocks.

The vast majority of the quartz grains shows undulatory extinction. This gives one reason to believe that the parent rock was not metamorphosed. The minor role of metamorphic rocks in the detritus supply can be discerned by the presence of only individual grains of staurolite and kyanite, which are indicators of the metamorphic process. The presence of a small amount of decomposed microcline, orthoclase, and acid plagioclase in the larger part of the section confirms the absence or very minor role of granitoids in the provenance areas.

The occurrence of Upper Visean sandstones, the reduction in grain size toward the southeastern part of the basin, the areal distribution of garnets in the region, and the presence of jaspilite debris in the southeastern subprovince suggest that several source areas have contributed detritus to the area under study at the north margin of the Dnieper-Donets Basin.

The main source area of detritus for subprovinces I and II was located in the northwest in Belorussia and on adjacent peneplains composed of older Paleozoic sedimentary and, less commonly, igneous rocks.

Marine Devonian deposits in the northwestern part of the Voronezh Massif exerted a great influence upon the formation of the southeastern terrigenous mineralogical subprovince. Some quantities of detritus were derived from outliers of ferruginous quartzites in the Belgorod iron ore region.

Detrital particles were transported toward the sedimentary basin by paleocurrents, which reached generally the boundary fault; then the sediments in marine, lagoonal-marine, and lacustrine basins were transported by predominantly littoral currents. For brief periods of time, however, there occur among the basin sediments beds of typical coarse underwater river drift (river-borne detritus) visible at a considerable distance from the shore. Commonly these strong currents carried unsorted, unrounded detrital material with a predominance of feldspar and igneous rock debris and with a presence of heavy minerals susceptible to transport and weathering. The source areas of this material were probably the individual blocks of magmatic rocks within the gradual submergence of the north margin of the basin.

The formation of subprovince III was linked to a further differentiation of detrital material of the first two subprovinces in a sedimentary basin farther away from the shore. In the most depressed part of the basin detritus of the aforementioned source areas mixed with old Paleozoic sedimentary rocks covering the Ukrainian Shield. The influence of magmatic rocks of the Ukrainian Shield on the formation of land-derived mineral associations of Upper Visean-Serpukhovian clastic rocks of the basin was less pronounced.

A determination of source areas and modes of transport of detrital materials is of fundamental importance in diagnosing lithologic, stratigraphic, and combination traps of hydrocarbons at the north margin of the Dnieper-Donets Basin.

1. The mineral compositions of both the light and the heavy minerals of the larger part of Upper Visean clastic rocks are represented by detrital components exceedingly resistant to weathering and transporting agents.

2. Unstable minerals occur in individual horizons.

3. At the north margin of the Dnieper-Donets Basin a rutile-tourmaline-zircon province has been defined, within which three subprovinces have been identified.

4. The main source areas of detritus were the old Paleozoic sedimentary rocks of Belorussia and the northwest slope of the Voronezh Massif.

In the most depressed part of the basin detritus of the aforementioned source areas mixed with old Paleozoic sedimentary rocks covering the Ukrainian Shield.

LITERATURE CITED

1. M. P. Kozhich-Zelenko, Lithology of Carboniferous Deposits of the Western Section of the Great Donets Basin [in Ukrainian], Vyd. Akad. Nauk URSR, Kiev (1961).
2. A. E. Lukin, Formations and Secondary Alterations of Carboniferous Deposits of the Dnieper-Donets Basin in Connection with Oil and Gas Resources [in Russian], Nedra, Moscow (1977).
3. "Use of paleogeographic methods of study in oil and gas explorations," Tr. VNIGRI, No. 278 (1969).
4. F. V. Shul'ga, Lower Carboniferous Coal-Bearing Formations of the Donets Basin [in Russian], Nauka, Moscow (1981).

B. F. Saltykov

UDC 550.4:553.492(477.62)

Based on a study of the distribution of trace elements in allophane-gibbsite ores of the Volga region, it is shown that these ores are independent of the rare-element composition of the sand-clay rocks of the bed roof, although they retain certain inherited features of carbonate and clay rocks in the bed floor. Literary data are summarized to compute the concentration clarkes of rare elements for alumina ores of chemogenic-sedimentary origin.

Rare elements are the classical indicators of petrogenetic and sedimentogenetic processes. Tenyakov [12, 13], in a generalization of the data on the distribution of trace elements in bauxites, showed that they are products of an extreme differentiation of aluminum and silicon enriched in hydrolysate elements. This process takes place only under hypergene conditions, when rocks experience weathering in a hot, humid climate. Tenyakov noted that any other way of Al and Si separation (such as aluminum transport by high-acidity waters) would immediately destroy this typical characteristic element association, as is observed in bauxitelike rocks.

These units are composed of Al and Fe hydroxides and aqueous aluminosilicates. Mikhailov [10] describes their distinctive features: depletion (up to total absence) of titanium, i.e., a disruption of the Al-Fe-Ti triad typical for bauxites, and the obligatory presence of allophane or halloysite as rock-forming components, as well as low trace-element contents and absence of all lithic structures. These features present these units as chemogenic sediments. High-alumina rocks of this kind have been discovered in Moscow region [10, 11, 14], Siberia [3, 15, 16], Volga region [2], and the Urals [4, 9].

Relevant data have been published in a few articles. In particular, Dombrovskaya [3] demonstrated, on a small number of specimens, that allophane-gibbsite rocks occupy an intermediate position in terms of the set of trace elements between the enclosing carbonate and aluminosilicate rocks. Quantitatively, they display heightened contents of Zn, Ni, and Co, due to sorption on poorly crystallized goethite. Ensov [4], describing bauxitelike rocks of Zhuravlinsk deposit (middle Urals), also notes a higher Ni and Cr concentration in some specimens. Both investigators suggest a hydrochemical theory of the formation of high-alumina rocks, i.e., an influx of alumina with sulfate water, although Dombrovskaya does not rule out a possible influx of aluminum with hydrothermal solutions. Mamaev [9] regards the combined accumulations of gibbsite and halloysite amid the terrigenous-carbonate rocks of south Urals as resulting from hydrothermal and solfatar argillization, and notes heightened concentrations of many of the trace elements characteristic for hydrothermal processes. A fluoride halo is observed along the perimeter of the ore bodies.

Geologists thus describe allophane-gibbsite rocks with various trace element compositions which owe their origins to diverse mineralization processes. At the same time, these entities are similar to the composition of sedimentary bauxites in the contents of their rock-forming components (alumina and silica). It is of interest in this context to compare the trace element composition of allophane-gibbsite rocks of various origins with those of bauxites. This study examines the allophane-gibbsite rocks of the Volga region.

The Don-Medveditsa dislocations are anticlinal structural elements of the southeastern slope of Voronezh anticlines; they are situated within the Volgograd region. Allophane-gibbsite rocks have been discovered in the northern and southern, most elevated portions of this structure. In both cases, the metalliferous formations are confined to lows of the roof of the Middle and Upper Carboniferous limestone, or occur amid a karst filling. Their occurrence settings have been studied best in Zhirnov (northern district), where an ore body has been mapped successfully in one of the open mines.

Geological Scientific Research Institute, Saratova State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 32-43, May-June, 1986. Original article submitted October 8, 1984.

TABLE 1. Associations of Trace Elements in Metalliferous and Enclosing Rocks of Zhirnov Area

Rock (no. of specimens)	Occurrence freq., %		
	80-100	50-75	30-45
Allophane-gibbsite ore:			
unaltered (100)	Mn-Ni-Co-Cu-Cr	Sr-Be	Sn-Zn-Ti-Ga
enriched in Mn (57)	Mn-Ni-Co-Cu-Cr-Zn	Sr-Ba	V-Pb
enriched in Ti (15)	Ti-Ga-Be		
sulfates of Al and Ca (17)	Ni-Cu-Sr-Ti	Mn-Co-Be	Cr
Roof (U_{3b}):			
clay (4)	Ni-Co-Cr-Cu-Sr-Ti-Ga	Mn-Pb	Zn
sand (5)	Ni-Co-Cr-Cu-V-Zn-Ti-Ga	Mn-Pb-Mo	Sn-Sr
Foot (C₁₋₄):			
carbonate meal (10)	Mn-Cu-Sr	Ni	Pb-Cr-Co-Ti-Be
limestone (14)	Sr	Mn-Ni	Co-Ti
clay (3)	Ni-Co-Cr-Cu-Sr-Ti-Ga	Mn-Mo	Zr

Allophane-gibbsite rocks form a lens-shaped body of a northwestern orientation, dipping very gently toward the southeast. Its thickness varies from 0.3 to 3 m, with a maximum in the middle. Down the section from the zone of solid ore, a veinlet-lens zone is observed, which occurs along the perimeter of the ore body penetrating a 5-7 m thick limestone layer. The veinlets range in thickness from a few centimeters to 1 m, and some converge to form lenses up to 1.5 × 15 m in size. All the allophane-gibbsite veinlets are localized along the limestone bedding planes; their overall thickness attains 2.5 m in the central part, diminishing to 1 m on the perimeter of the ore body.

The contacts of individual veinlets and the solid ore zone with the enclosing carbonate rocks are sharp and distinct. The alteration of the carbonate rocks includes partial bleaching, ferrugination, and manganization. In rare cases, limestone is replaced intensely by early gypsum or cryptocrystalline gypsite; the contact is then only observed in polished section, while the rock has a porous appearance with an indistinct stratification.

The allophane-gibbsite rocks in the solid ore zone occur on an uneven, slightly karsted, limestone surface. As the zone becomes thicker, the gypsometric level of the limestone row becomes lower, and the limestone layers are cut across by metalliferous rocks. The roof of the ore body also has an uneven surface due to erosion. The ore is usually overlain by Bajocian sand. Frequently, they lie on a basal horizon of quartzose pebblestone, sometimes converted to a conglomerate with ferruginous cement. Up the section, grey hydromica-montmorillonite Bajocian clay occurs.

Allophane-gibbsite rocks have the appearance of an earthy mass of an ochre color with multiple white nests and lenses formed of the same minerals (gibbsite and allophane), although with no iron hydroxides. Most are localized at contacts with limestones, which not only underlie the ore body, but form residuals within the zone of solid ore.

The following minerals are identified among the metalliferous rocks; principal minerals: gibbsite and allophane; secondary: boehmite, nordstrandite, alumohydrocalcite, hydrogoethite, halloysite, and lithioforite; and accessory minerals: gypsum, aluminite, basaluminite, yaro-site, and alunite. Relict calcite and dolomite occur in minor amounts as small corroded fragments or, more often, as carbonate powder scattered amid the groundmass. Immersion investigation determined an exceptionally poor set of terrigenous minerals. The light fraction contains, in addition to predominant allophane and gibbsite, single traces of quartz and feldspar grains, angular flint fragments, and spherical montmorillonite clay units colored brown-ochre by the finely dispersed goethite and penetrated with microscopic gypsum crystals. The heavy fraction consists mainly of iron and manganese hydroxides with rare signs of zircon, rutile, epidote, disthene, staurolite, tourmaline, and siderite. All of these terrigenous minerals are not found in any particular specimen; only the first three are found in limestone.

In the southern part of Don-Medveditsa dislocation, near Frolov, high-aluminum rocks are found amid a karst filling, where they form a small nest and, less frequently, lens-shaped bodies, 0.1 × 2.5 m in size. They contain gibbsite, allophane, halloysite, and secon-

TABLE 2. Mean Contents of Trace Elements in Allophane-Gibbsite Ores and Enclosing Rocks, g/ton

Rock, segment	Seg- ment	No. of speci- mens	Mn	Ni	Co	Cr	V	Pb	Cu	Zn	Ba	Sr	Ti	Ga	Be
Allophane-gibbsite ore:															
unaltered	Z	100	200	100	20	80	3	—	30	40	—	120	90	1	8
	F	4	200	400	145	40	55	—	75	—	550	300	650	1	—
enriched in Mn	Z	57	4000	300	200	40	—	—	25	60	—	250	150	1	15
enriched in Ti	Z	15	250	210	50	120	8	2	70	110	100	120	1000	5	4
sulfates of Al and Ca	Z	17	150	70	10	20	—	—	20	—	—	700	450	—	10
	F	2	—	40	20	120	—	—	75	40	—	450	1000	—	—
Roof sediments (J ₂ b)															
clay	Z	4	100	80	15	120	80	10	80	80	—	250	3100	6	2
sand	Z	5	300	100	40	100	15	10	60	80	—	70	5300	10	—
Foot (C ₂₋₃)															
carbonate meal	Z	10	150	80	2	20	10	5	20	—	—	400	350	1	3
	F	15	100	15	5	—	—	—	12	—	—	250	170	—	—
dense limestone	Z	14	400	20	5	10	—	—	—	—	50	650	100	—	1
	F	11	70	—	—	—	—	—	—	—	—	400	70	—	—
montmorillonitic clay	Z	3	100	60	5	30	—	—	30	—	—	200	1000	4	—
	F	9	160	160	9	60	45	7	65	—	120	130	3300	7	26

*Segment: Zh — Zhirnov; F — Frolov

dary alunite and yarosite. In view of the similarity of the mineral composition and perfect analogy of occurrence settings with similar units observed in the karst filling of the Zhirnov area, in the immediate vicinity of the ore body described above, the two can be assumed to be of the same genetic origin.

Trace elements in rocks were determined by a quasi-quantitative spectral investigation at the laboratory of Geological Research Institute of Saratov University (analysts L. N. Nikitina and F. D. Adesman), who used an ISP-26 spectrograph and a sieve-through process. The elements W, Bi, Y, Ce, La, Cd, Sc, Ag, Sb, Ta, Nb, Ti, and Ge were not discovered in any of the specimens, while Mo, Zr, and Sn were recorded in a few of the specimens in quantities near the sensitivity of the method ($\approx 10^{-4}\%$). The results of the analysis for the other trace elements are given in Tables 1 and 2.

The allophane-gibbsite rocks have been subdivided into groups for convenient description of the distribution of trace elements: a) white, off-white, light-ochre rocks, which form the bulk of the ore body, are described in the tables as unaltered; b) high-manganese rocks with a characteristic grayish color and, in the case of a very high Mn concentration, gray and dark gray (in the section, they are distributed unevenly as small nests; only close to limestone contacts they form small lenslike zones that are traceable into the limestone as well); c) rocks enriched in titanium with a brownish color due to the presence of amorphous lumps or spherical units of montmorillonite, clay, and hydrogoethite (confined to the lower portion of the solid ore zone as separate nests, but not found as veinlets or lenses amid limestone); d) secondary aluminum and calcium sulfates, forming small nests and fine veinlets across all earlier minerals.

By frequency of occurrence of the trace elements, the rocks are subdivided into three groups (see Table 1); each is characterized by an association of trace elements of its own. The first two groups frequently include an association of most mobile Mn, Ni, Co, and Cu and less mobile Cr [1, 8]. Zn, Ti, and Ga occur here sporadically; no Zr has been found. In high-titanium rocks, hydrolysat elements are found in almost every specimen, and in some, Ba, V, and Pb are also recorded. For Al and Ca sulfates, an entirely different set of trace elements is typical, underscoring their secondary nature relative to the ores.

The enclosing limestone differs drastically from the alumina ore by the set of trace elements. The dense varieties often contain only strontium. Manganese and nickel are seen only in specimens from contacts with the ore body. As solid limestone is converted to carbonate powder, which forms lens-shaped interlayers, conformable to the bedding planes, Mn and Cu join Sr.

TABLE 3. Correlations of Elements in Volga Region Ores

Ore	No. of specimens	Mn-Ni	Mn-Co	Ni-Co	$\rho_{0,08}$	No. of specimens	Fe ⁺⁺ -Mn	Fe ⁺⁺ -Ni	Fe ⁺⁺ -Co	$\rho_{0,08}$
Unaltered	100	0,45	0,58	0,51	0,19	23	0,28	0,56	0,41	0,42
Mn-enriched	57	0,41	0,66	0,30	0,26	17	0,34	0,52	0,04	0,48

TABLE 4. Contents of Trace Elements in Volga Region Goethites, g/ton

Specimen No.	Mn	Ni	Co	Cr	Mo	Cu	Zn	Sr	Ba
3/4	—	40	3	10	—	3	—	—	—
35/87b	1000	200	100	20	—	80	1000	100	2000
B-4b	800	100	60	20	—	40	800	—	1000
B-9b	450	100	40	20	—	40	800	—	800
B-10b	2000	300	600	10	—	60	3000	100	2000
B-11a	1500	200	300	10	—	30	1000	—	1000
Mean	1000	160	180	15	—	40	1100	60	1200
505-10 [3]	No data	500	500	—	20	5	1000	100	—

Lens-shaped interlayers not thicker than 30 cm, of yellow montmorillonitic clay, are observed amid limestone; their trace element set is similar to that of the Jurassic hydromicaceous-montmorillonitic clay in the roof of the ore body. Both are characterized by an association of mobile (Ni, Co, Cu, Sr) and low-mobility (Cr, Ti, Ga, Zr) elements. In the Jurassic sand, V and Zn are also present.

A comparison of allophane-gibbsite and the surrounding sand-clay rocks (including C₂₋₃) by the set of common trace elements shows that the mobile elements are present in all of them. The distinction is seen primarily in the absence of low-mobility components, except for chromium, in the ore. High-titanium ores, in that respect, are similar to clay. Remarkably, vanadium is characteristic for the ore of Frolov area, which is also found in Carboniferous clay. Allophane-gibbsite rock differs significantly from limestone in the set of trace elements. When they become carbonate powder, the trace element composition comes closer to that of the ore.

These data cause us to disagree with Dombrovskaya [3], who believes that allophane-gibbsite rocks have a trace element set that is intermediate between those of carbonate rocks and aluminosilicate rocks. The ores in the Volga region exhibit trace elements most mobile in humid conditions, which makes them similar to sand-clay sediments of the roof; the almost complete absence of hydrolysate elements is their distinctive feature. The ore differs clearly from limestone in the trace element set, although geologic observations have determined metasomatic substitution of allophane and gibbsite for calcite.

A comparison of the main contents in the samples (see Table 2) reveals patterns suggestive of the settings in which allophane-gibbsite rocks originated.

1. As solid limestone becomes carbonate powder, Ni, Ti, Be, and Cr concentrations rise, small quantities of V, Pb, Cu, and Ga appear, while Ba and Sr contents diminish. Mn and Co concentrations vary in tandem, but this variation has no regularity in different areas, due to uneven distribution of manganese. A comparison with allophane-gibbsite rocks suggests that this alteration took place concurrently with the formation of the ore, which is responsible for a slight increase in the contents of certain elements with a simultaneous loss of Sr and Ba typical for carbonate rocks. This hypothesis is supported by the presence of powdery relict calcite amid aluminum ore localized in lenses and veinlets, which sometimes displays a gradual succession from alumina-rich matter to a relatively pure carbonate powder, especially along the perimeter of the ore body.

2. The trace element distribution in allophane-gibbsite rocks of the Zhirnov and Frolov areas are different. In the former, unaltered ore, despite the proximity of medium concentrations of certain elements (Mn, Ni, and partly Co and Sr), still retains an independent trace element set unaffected by the enclosing sand-clay rocks of both the roof and the floor. At the same time, an indistinct inheritance of the rare elements of the ore from carbonate rocks can be observed. Compared with the carbonate rocks, the ore accumulates Ni, Co, Cu,

TABLE 5. Correlation of Trace Element Contents in Allophane-Gibbsite Rocks of Volga Region, Urals, and Baikal Region, g/ton

Region	Mn	Ni	Co	Cr	V	Pb	Cu	Zn	Ba	Sr	Ti	Ga	Be	Mo	Zr
Volga	200 4000	100 300	20 200	60 120	3 8	— —	30 70	40 110	— 100	120 250	900 1 000	1 5	4 15	— —	— —
Middle Urals [4]	100	30—1000	10	30—1000	30—60		30—300	30—300	100	100	100—500	10	no data	30	30— 100
Baikal [3]	600	900	100	30	30	—	20	500	30	—	1 000	—	»	4	50
Probable concentra- tion clarke	800	400	100	60	10	2	50	100	100	100	500	5	5	10	50
South Urals [9]	no data	n000	n00	no data	no data	n00	n00	n000	n000	no data	1 000	no data	n00	n00	
Genetic classes of bauxite deposits [13]:															
eluvial	600	22	21	623	173	26	35	46	30	30	21 000	49	2,3	8,0	647
sedimentary	400	70	30	424	312	44	56	103	60	150	17 000	50	2,6	8,6	417
karst	800	137	36	547	393	67	51	115	90	230	14 000	55	7,0	8,1	518

Zn, Cr, and Be and loses Sr, Ba, Ti, and Ga. Dombrovskaya has made similar observations [3].

The Frolov area reveals the inherited nature of the trace element composition of the ore, originating from the Carboniferous clay more clearly; the allophane-gibbsite rocks are enriched in mobile elements (Mn, Ni, Co, Ba, Sr), and depleted in hydrolysate elements (Ti, Ga, Be, Zn, Pb), while the concentrations of Cr, V, and Cu are the same. Remarkably, the ore in this area includes vanadium, fully inherited from the clay; in Zhirnov ore, much smaller amounts of this element (by more than an order of magnitude) are found. A slightly heightened titanium content as compared with the Zhirnov area probably also has the same cause.

The distribution features of trace elements in Zhirnov ore suggest that this ore cannot be regarded as a residual formation originating from the alteration of the clay matter of the roof; this is confirmed by geologic observations. The clay filling of the Frolov karst probably was the main contributor to the allophane-gibbsite ore, especially since, according to experimental data [6], montmorillonite is susceptible to decay with the loss of silica in alkaline medial carbonate rocks, particularly in the presence of organic acids in drained natural waters. In that case, however, one cannot say that a trace element set of the ore has been inherited from Carboniferous clay.

3. The allophane-gibbsite ore with a higher Ti content as compared with unaltered varieties also has heightened concentrations of almost all trace elements, with the sole exception of Sr and Ba, which are present in smaller amounts. A comparison of the trace element set of the rocks of this group with Carboniferous clay indicates that the contents of Ti and Ga which are inert in humid conditions remains unaltered, the concentrations of more mobile elements (Mn, Ni, Co, Cu) increase by a factor of 3-10, while Sr is washed out. Maximum quantities of a number of elements (V, Pb, Cr, Zn, Ba, Be) discovered in ore are registered in these rocks. These distribution features and the finds of rare quartz and feldspar grains and spherical rounded pellets of montmorillonite clay indicate that the disparate accumulations of this rock amid the groundmass of the ore body are relics of terrigenous (clay) sediments (probably also Carboniferous clays), which provided the parent matter by bauxitization on a carbonate bed during the formation of at least a part of the ore body.

Bauxitization of montmorillonitic clay in alkaline settings of carbonate rocks is observed in both areas. In Zhirnov, these processes play a limited role in ore formation against the background of predominantly chemogenic precipitation; at Frolov, on the contrary, bauxitization prevails, probably due to the specific karst environment. The similarity of trace element composition of the ores in these areas, however, emphasizes their genetic affinity. This fact, and the shortage of material on Frolov area, give hope that expanded exploration will reveal Zhirnov-type alumina ores in the southern part of Don-Medveditsa dislocations as well.

4. Allophane-gibbsite rocks enriched in Mn have higher concentrations of Ni and Co, and, to a lesser extent, Sr, Be, and Ti than in unaltered rocks. Dombrovskaya [3] believes that the increased Ni, Co, and Zn contents in metalliferous rocks of the Baikal region is due to sorption of these elements on goethite. For testing this hypothesis, we have computed correlations (Table 3) and carried out analysis of goethite single fractions from Volga region ores (Table 4).

The findings indicated a medium-strength correlation for the Mn-Ni pair, which varies little in the rocks of groups "a" and "b." Similar results were obtained also for Fe^{3+} -Ni, except that the correlation was somewhat stronger. It appears that Ni accumulates along with Mn or Fe^{3+} with equal probability. In the Mn-Co pair, the correlation is stronger, and increases in the rocks as one passes from group "a" to group "b." Cobalt forms a weak correlation with Fe^{3+} (group "a"); this linkage disappears in Mn-enriched rocks, i.e., Co accumulates mainly together with Mn, while its association with iron in group "a" rocks is probably due to the presence of Mn minerals amid goethite accumulations. In Mn- Fe^{3+} pair, no significant correlation was observed.

The possibility of concurrence of Mn and Fe minerals in rocks is based on the following considerations. The data of Table 4 indicate that Mn contents in goethite single fractions attain 2000 g/ton, although, in isolated specimens, Mn may be absent. Geological observations have established that when Mn minerals accumulate mainly in the ore at the limestone boundary, high Fe_2O_3 contents are recorded at the top of the ore body. Poorly crystallized goethites are known to have a high sorptance. A partial combined accumulation of Mn and Fe is, therefore, possible, although an oxidative environments ($\text{Eh} < 0.4 \text{ B}$) Fe^{3+} precipitates

from the solution before Mn, which is released into sediment at pH 8 [7]. Burkov [1], in an investigation of the trace element paragenesis in sedimentary beds, also notes the disappearance of Mn/Fe correlation as one passes from arid settings (alkaline water) to humid settings (mainly water with pH <7), especially in the presence of chemical weathering.

In the Volga region, the alumina ores contain, as a mineral, lithiophorite, which has a gibbsite-type texture [17], precluding the presence of large amounts of Ni and Co (as distinct from asbolane). The formation of lithiophorite presumes the presence of seminal gibbsite in the solution, caused by a decay of organomineral Al complexes. As the mineralization area dries out, Mn^{3+} , migrating in the water, is oxidized to Mn^{4+} , which forms the mineral. The chemical analysis of manganese accumulations in the Volga region indicated the presence of only Mn^{4+} ; the divalent form has not been found.

The following conclusions can be drawn:

1) Although Fe^{3+} and Mn are separated during the course of mineralization, the latter precipitates later than the former, and migrating in a solution filtering through the rock, can be sorbed partially by poorly crystallized goethite. Along with Mn, an amount of Ni and Co would probably also be sorbed. In addition, isomorphous occurrence of Ni and Co in goethite is possible, because these elements can form ROOH compounds, isostructural to goethite. Correlation data, however, suggest that Ni can be accumulated equally by Fe and Mn minerals, while Co clearly gravitates toward Mn, as emphasized by complete disappearance of Fe-Co correlation in the rocks of the group "b." The maximum Ni and Co contents in these rocks are 3000 and 1000 g/ton, while in goethite, they are not higher than 300 and 600 g/ton, with the inevitable increase of Mn concentration (see Table 4); 2) Increased Ba contents in goethite are also accompanied by increased Mn content, although in group "b" rocks, Ba is present in minute amounts. This distribution may be linked with the most oxidized Mn forms occurring at the top of the profile, where ferrugination is more intense. These Mn forms give rise to cryptomelanes and todorokites with large channels containing major Ba type cations ($r = 1.38 \text{ \AA}$) [17]. The probability of occurrence of these minerals in the Volga region is based on identification of reflections on diffractograms. Chukhrov et al. believe that lithiophorite, cryptomelane, and todorokite can precipitate from the same solutions, and occur in close associations in ores of different compositions; 3) Accumulation of Zn apparently results from goethite sorption, as suggested by Dombrovskaya [3], although Mn minerals may contribute to that process as well. A high sorbance of low-valence Mn oxides in relation to Zn has been established experimentally [21] (Cu, Co, and Ni cations had a susceptibility to sorption that was lower by a double-digit and triple-digit factor). With increasing manganese valence, Ni and Co are accumulated more than zinc; 4) The enrichment of allophane-gibbsite rocks in the characteristic trace elements is thus determined by sorptive and isomorphous processes. The main part belongs to Mn minerals, which increase the Co, Ba, and partly Ni, concentrations. A portion of Ni and Zn may be sorbed by poorly crystallized goethites.

5. Compared with alumina ores, lower Ni, Co, and Cr, higher Sr and Ti, and equal Mn, Cu, and Be concentrations are observed for Al and Ca sulfates. The trace element sets and the amounts of these elements are suggestive of some inheritance from the enclosing limestone and the alumina ores with a slight influx of titanium. For heavily oxidized sulfate water, Yakovleva [18] demonstrated the potential transport of this element. The differences in the distribution of trace elements in allophane-gibbsite rock and secondary sulfate contradict the assumption that sulfate waters were the main vehicle in aluminum migration. This is also supported by absence or poor development of early gypsum in allophane-gibbsite paragenesis, which is indispensable for the precipitation products of sulfuric acid weathering.

A COMPARISON OF THE TRACE ELEMENT COMPOSITIONS OF ALLOPHANE-GIBBSITE ROCKS AND BAUXITES

All the factual data available in the literature on trace element contents in allophane-gibbsite rocks and their mean concentrations in bauxites are summarized in Table 5. Most publications give concentration ranges, but do not indicate the mean levels, which makes it difficult to compare the trace element compositions. Table 5 for the Volga region gives the mean concentrations of elements in unaltered rock (top line) and maximum mean values in rocks of groups "b" and "c" (bottom line). Based on Dombrovskaya's data, the mean element contents in Baikal region ores have been estimated.

When the trace element sets of allophane-gibbsite rocks are compared for Volga region, middle Urals, and Baikal region, the mean concentrations of almost all elements are similar or at least comparable in order of magnitude. For the metalliferous rock, high contents of Mn, Ni, and Co, the absence of Pb, and low concentrations of Cu, Cr, V, Ga, Ti, Ba, Sr, Zn, Mo and Zr are typical, although in isolated specimens, somewhat higher V, Cr, Zn and Cu concentrations may be observed. This is probably due to an increased role of bauxitization of clay rocks on a carbonate bed, as was mentioned above for Frolov ores. Bauxitelike rocks of Kaluga province have concentrations of hydrolysate elements (Ti, Zr, and Cr) higher by a factor of 1.5-3.5 than the infiltrational allophane-gibbsite ores of Tula and Ryazan provinces [5]. Bauxites, on the other hand, have low contents of Co, Ni, Cu, and Be, typical for infiltration formations. Zubkovskaya notes this basic difference, showing that Kaluga kaolinite-gibbsite ores are products of mechanical transport of matter from decaying lateritic crusts of weathering of a pre-Visean age.

A discrepancy in the trace element contents in metalliferous rocks from different regions may be due to nonuniformity of the material analyzed, and particularly, the difficulty of isolating rock specimens with traits of sulfuric-acid weathering from the samples. As we have demonstrated, these processes cause significant redistribution of trace elements, with the creation of different qualitative and quantitative associations.

Despite the scarcity of factual material, we attempted to estimate the concentration clarkes of rare elements in allophane-gibbsite rocks of a chemogenic-sedimentary origin (see Table 5); these data provide a benchmark for comparing these entities among themselves, and also with bauxites.

Allophane-gibbsite rocks of the south Urals, which are assumed to be of a hydrothermal-sulfataric origin [9] differ drastically in the trace element content from the units described above, primarily by high concentrations of elements typical for hydrothermal processes (Pb, Zn, Ba, Be, Mo, La, As). Titanium contents, however, are rather low in them. This distribution, according to Mamaev, is attributed to the fact that allophane (halloysite)-gibbsitic argillisite represents the rear zone of metasomatic column, developed after titanium-depleted clay limestone. Tenyakov [12] noted the possibility of accumulation of such characteristic elements in a discussion of the potential for hydrothermal formation of bauxite. Argillisites in this case differ from bauxites by a heightened content of these elements, which is higher by one to three orders of magnitude in them.

Compared with bauxite, allophane-gibbsite rocks of a chemogenic-sedimentary origin have near concentrations of Cu, Zn, Ba, Sr, Be and Mo, heightened contents (sometimes by an order of magnitude) of Mn, Ni, and Co, and a drastic depletion (by one or two orders of magnitude) in the hydrolysate and ore-forming elements (Cr, V, Pb, Ti, Ga, Zr, etc.); these differences are less pronounced for geosynclinal bauxites, localized amid carbonate rocks.

Aluminum formations, thus, can be subdivided by trace element composition into three groups: 1) bauxites with hydrolysate element accumulations; 2) hydrothermal argillisites significantly enriched in elements typical for hydrothermal processes; and 3) chemogenic-sedimentary allophane-gibbsite rocks depleted in most trace elements, but with obligatory accumulations of Mn, Ni, Co, and partially Zn.

* * *

The comparative analysis of the distribution of trace elements has revealed the features separating chemogenic-sedimentary allophane-gibbsite rocks from both bauxites and hydrothermal argillisites; this gives grounds for rejecting the theory of their origin from bauxite-forming (lateritic crust of weathering or terrigenous transport of bauxite material) and hydrothermal processes.

In none of the regions where these formations are found have any traces of hydrothermal alteration of the enclosing rocks been observed, and no direct correlation with crusts of weathering has ever been established.

The localization environments of allophane-gibbsite ores and the correlations of the minerals indicate successive precipitation of material from solutions. Experimental investigations and analysis of natural waters suggest two likely forms of aluminum transport: as alumofulvate complexes or in strongly acid sulfate solutions. At the moment, it is impossible to establish definitively the reliable features for distinguishing between these two methods of transport for identifying their effects in the formation of allophane-gibbsite rocks. Judging by in vitro studies of Al_2O_3 - SO_3 - H_2O systems [19, 20], an increase of solution

pH leads to the precipitation of a basic aluminum sulfate rather than gibbsite. In situ, aluminum sulfate associates with gypsum and iron sulfate, and the gypsum is often the predominant mineral. In allophane-gibbsite rocks, Al, Ca, and Fe sulfates in all occurrence areas are secondary minerals, often separated in formation time from the basic mineralization process. Studies of trace elements in Volga region ores also indicate their redistribution during the formation of Al and Ca sulfates. The sulfuric-acid weathering is, therefore, more likely a superimposed process causing a decay of allophane-gibbsite rocks.

An influx of aluminum in the form of organic-mineral complexes is probable for alumina rocks of the Moscow region [10, 11]. In the Volga region, this mechanism of alumina transport is also most likely. The distribution of trace elements in the ores of this region suggest that they are independent of the rare-element composition of the sand-clay rocks of the roof, although some traits of inheritance from carbonate and clay rocks of the bed floor have been noted. It is possible that the formation of allophane-gibbsite rocks in the Don-Medveditsa dislocation resulted from two main processes: 1) direct precipitation of matter from solutions neutralized on contact with limestone, and 2) bauxitization of clay material remaining after the dissolution of carbonate rocks or introduced by the same solutions as suspended matter precipitated during the filtration through limestone, as a result of colmatage. This scheme of allophane-gibbsite rock formation is consistent with the geological and mineralogical observations, so that trace elements in this case, too, function as indicators of mineralization processes.

LITERATURE CITED

1. Yu. K. Burkov, "Linear parageneses of minor elements in sedimentary strata as indicators of sedimentogenesis settings," in: Physical and Chemical Processes and Facies [in Russian], Nauka, Moscow (1968), pp. 22-26.
2. Yu. V. Van'shin, V. A. Gutsaku, V. F. Saltykov, and A. F. Chernyaeva, "Geology and material composition of aluminum ore deposits in the Volga region," in: Bauxite Deposits and Their Association with Weathering [in Russian], KazIMS, Alma-Ata (1983), pp. 182-192.
3. Zh. V. Dombrovskaya, "The origins of allophane-gibbsite mineralization in the rocks of the Baikal series (Western Baikal region)," in: Crusts of Weathering [in Russian], Vol. 16, Nauka, Moscow (1978), pp. 89-106.
4. G. I. Entsov, "'Lower Carboniferous' bauxites of the western slope of Middle Urals," Geol. Rud. Mestorozhdenii, No. 6, 94-101 (1982).
5. E. I. Zubkovskaya, "Mineralogy of bauxites from Southwestern Moscow syncline," Byul. MOIP, Otd. Geol., No. 6, 135 (1974).
6. D. Carol and H. C. Starkey, "Lixiviation of clay minerals in a limestone environment," in: Geology and Mineralogy of Bauxites [Russian translation], Mir, Moscow (1964), pp. 465-471.
7. K. B. Krauskopf, "Separation of manganese and iron in the sedimentary process," in: Geochemistry of Lithogenesis [Russian translation], IL, Moscow (1963), pp. 259-293.
8. N. A. Lisitsyna, "The washout of chemical elements during the weathering of basic rocks," Tr. GIN AN SSSR, No. 231, 224 (1973).
9. I. N. Mamaev, "Argillization of terrigenous-carbonate rocks in the western slope of South Urals and genesis of combined gibbsite and halloysite accumulation," Litol. Polezn. Iskop., No. 1, 17-29 (1982).
10. B. M. Mikhailov, "Geological premises for detection of chemogenic and volcanogenic-sedimentary deposits of alumina," in: New Nonbauxite Types of Alumina Raw Materials [in Russian], Nauka, Moscow (1982), pp. 91-99.
11. E. V. Mikhailova, "Bauxite deposit zone in the southern margin of Moscow basin," in: Materials on Geology and Mineral Resources of the Central European Part of the USSR [in Russian], Vol. 1, Moscow (1958), pp. 215-227.
12. V. A. Tenyakov, "The sources and methods of bauxite matter formation (geochemical aspects)," in: Problems of Bauxite Genesis [in Russian], Nauka, Moscow (1975), pp. 18-31.
13. V. A. Tenyakov, "Bauxites of the principal genetic classes: Correlation of major geochemical characteristics," in: Bauxite Deposits and Their Correlation with Weathering [in Russian], KazIMS, Alma-Ata (1983), pp. 28-39.
14. K. N. Trubina, "Bauxite-bearing deposits of the Moscow basin," in: Bauxites: Their Mineralogy and Genesis [in Russian], Izd. Akad. Nauk SSSR, Moscow (1958), pp. 335-346.
15. G. N. Cherkasov, "Geology, composition, and genesis of bauxite and gibbsite-allophane rocks of Western Yakutia and Baikal region," Lithol. Polezn. Iskop., No. 6, 120-127 (1978).

16. G. N. Cherkasov, B. G. Kraevskii, V. I. Bgatov, et al., "Gibbsite-allophane deposits of Central Altai-Sayan region," Tr. SNIIGGIMS, No. 235, 49-54 (1976).
17. F. V. Chukhrov, A. I. Gorshkov, A. V. Sivtsov, and V. V. Berezovskaya, "The mineralogy of manganese in lateritic weathering products," Izv. Akad. Nauk SSSR, Ser. Geol., No. 8, 87-100 (1982).
18. M. N. Yakovleva, "Geochemistry of aluminum, titanium, iron, and silicon in a sulphuric acid weathering environment (in conjunction with the origin of bauxites)," in: Bauxites: Their Mineralogy and Genesis [in Russian], Izd. Akad. Nauk SSSR, Moscow (1958), pp. 120-161.
19. M. N. Yakovleva, N. V. Saprykina, and G. A. Sidorenko, "The possibility of coprecipitation of aluminum hydrate and silicic acid in the Al_2O_3 - Na_2O - SiO_2 - SO_3 - H_2O system during the variations of pH values (in connection with the origins of bauxites)," Mineral'noe Syr'e, No. 2, 131-143 (1961).
20. R. H. Hsu and T. F. Bates, "Formation of x-ray amorphous and crystalline aluminum hydroxides," Mineral. Mag., 33, No. 264, 749-768 (1964).
21. R. M. McKenzie, "The sorption of some heavy metals by the lower oxides of manganese," Geoderma, 8, No. 1, 29-35 (1972).

LOWER PROTEROZOIC CUPRIFEROUS FORMATIONS OF THE UGUI TROUGH,
SOUTH YAKUTIA, AND THEIR CORRELATION WITH THE UDOKAN COMPLEX

Yu. V. Davydov

UDC 553.43:551.72(571.56)

In considering material composition of Lower Proterozoic deposits in South Yakutia, evolution of rock from volcanic sedimentary and arkosic to feldspar-quartz and then to graywacke is demonstrated. It is traceable also from their petrochemical features. Analysis of thicknesses, chemical composition, and absolute age data correlates these deposits with the upper part of the Udokan complex.

The Ugui graben trough in the western part of the Aldan shield has a fill of Lower Proterozoic deposits. It is similar to the familiar Udokan trough but smaller in size (Fig. 1). As of now, there is no unity of opinion on tectonics of these structures and consequently of the formation association of their sedimentary fill. Some investigators [5-7, 10, 24, 25] identify these structures as belonging to the Proterozoic platform, in the belief that the graben-shaped troughs are geosynclinal troughs or else paleoaulacogens. According to some students [2, 16, 19], Udokan formations near the Aldan and Chara platforms are miogeosynclinal; others [3, 8, 11] regard the Lower Proterozoic formations as orogenic, developed in the intermontane troughs.

The Lower Proterozoic deposits of the Ugui trough are of interest because they, like those of the Udokan trough, are cupriferous. In recent years, field work of subdivisions of the PGO "Yakutskgeologiya" and Yakutian Affiliate, Academy of Sciences of the USSR, including exploration drilling, has yielded new information on the geology and copper potential of deposits in the Ugui trough.

THE SECTION

Lower Proterozoic deposits of this structure make up a large transgressive-regressive cycle consisting of the lower red, carbonate-tuffaceous-terrigenous sequence; middle gray, carbonate-terrigenous; and upper, red, terrigenous deposits. The lower sequence consists of the Olonga carbonate and Tuostai tuffaceous-terrigenous suites; the middle sequence is known as the Choruod suite; and the upper - as the Kebekta suite.

Institute of Geology, Yakutian Affiliate, Siberian Division, Academy of Sciences of the USSR, Yakutsk. Translated from *Litologiya i Poleznye Iskopayemye*, No. 3, pp. 44-58, May-June, 1986. Original article submitted March 30, 1984.

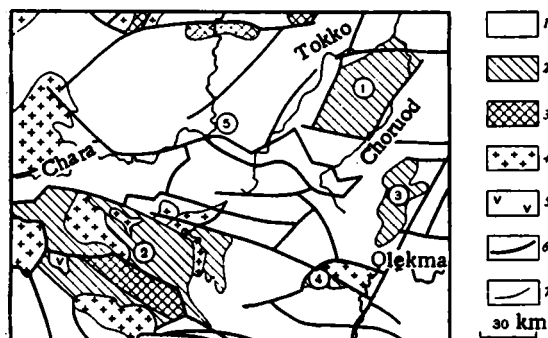


Fig. 1. Tectonic map of western part of the Aldan shield [22]. Formations: 1) Archean metamorphic; 2) Lower to Middle Proterozoic sedimentary; 3) Upper Proterozoic sedimentary; 4) Lower to Middle Proterozoic granites; 5) Middle Proterozoic gabbros; 6) faults; 7) geologic boundary. Encircled numerals: 1) Ugui trough, 2) Udokan trough, 3) Oldongsa trough, 4) Khana trough, 5) Olekma-Chara uplift.

The Olonga suite was identified in 1971 by V. N. Salatkin [15] in the lower reaches of the Choruod River. Its base of gray to varicolored, mixed-grain, slightly carbonate, arkosic sandstones with stringers of gravelstones and small-pebble conglomerates rest erosionally upon Archean rocks. They are replaced higher up the section by pink-gray, bordeaux, and gray, massive, thick-tabular, manganesian dolomites with 2-5 m thick, bordeaux-colored to gray, jasperlike cherts. Total thickness of the suite, 80 m [1, 15].

The Tuostai suite, developed in the eastern part of the Ugui trough [1, 15], was formerly assigned to the Namsala suite [11-14], with the type section in the Oldongsa trough and consisting of two horizons of different rocks. The first (lower) horizon is an alternation of cherry-colored tuffites and tuffaceous siltstones, sandstones, and gravelstone-conglomerates. The second (upper) horizon consists of cherry-colored, arkosic sandstones with stringers of gravelstone-conglomerates at the base (Fig. 2). The most complete, unbroken section of this suite, 109 m thick, although without the basal beds, was penetrated by drillhole 9, in the Usuu segment.

The Choruod suite of the Ugui trough differs greatly from the under- and overlying Tuostai and Kebekta suites by its lithological and geochemical features: gray coloring of its deposits, their substantial carbonate content, mineralogical and structural maturity* of the sandstones, enrichment in organic carbon, and finally a cupriferous character of the suite.

This suite is subdivided into three horizons. The first (lower) one is an alternation of dark-gray, gray, and light-gray quartz and arkosic sandstones, siltstones, and dolomites. The second (middle) horizon is represented by light-colored, monomineral quartz sandstones. The third (upper) horizon consists of black, dark-gray, and reddish, sandy brecciated dolomites and dolomitic sandstones (Fig. 2). The facies of this suite are extremely inconsistent, in horizons of variable thickness. Particularly inconsistent are deposits of the first and third horizons, which prevents their identification as a suite. The total thickness of this suite varies from 140 to 220 m.

The Choruod suite partly corresponds in volume to the Choruod series of the Biryulkin et al. stratigraphic chart [2]. According to that chart, the Choruod series is subdivided into the Pravda suite of quartz sandstones and the Amnuna suite of varicolored, cherty dolomites and marls. Corresponding to the Pravdinsk suite in our chart is the second horizon of the Choruod suite. The third horizon evidently is a stratigraphic analog of the Amnuna suite. The Biryulkin chart does not contain stratigraphic analogs of the first Choruod horizon.

*Structural maturity is determined by the degree of rounding, sorting, and rinsing of the sand grains from the argillaceous material.

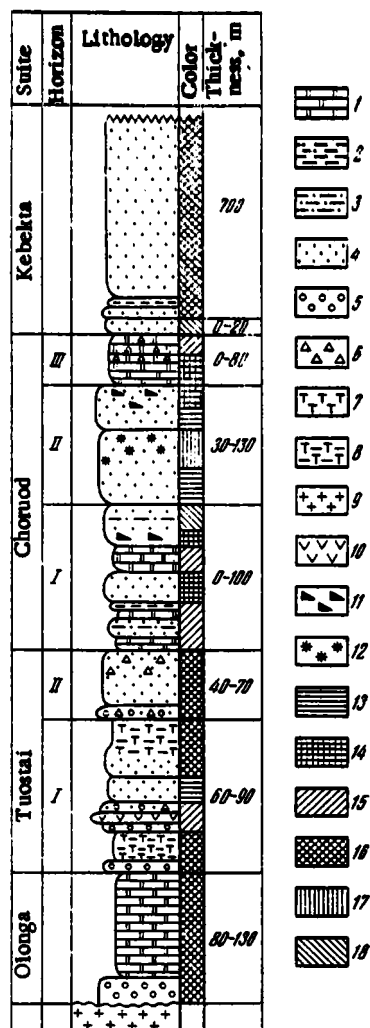


Fig. 2. Composite Lower Proterozoic section of the Ugui trough: 1) Dolomites; 2) argillites; 3) siltstone; 4) sandstones; 5) conglomerates and gravelstones; 6) breccias and conglomerate-breccias; 7) tuffites; 8) tuffaceous siltstones; 9) granites; 10) diorite-porphyrries; 11) bituminosity; 12) pockets of iron hydroxides. Rock coloring: 13) light-gray; 14) dark-gray to black; 15) pink; 16) red, cherry-red, cherry; 17) gray; 18) greenish to gray-greenish.

The Kebekta suite comprises the most widespread, well-exposed sedimentary formations of the Ugui trough: a monotonous sequence of consistent facies of red sandstones, mainly fine-grained, slaty. Their boundary with underlying sediments of the Choruod suite, is vague in northern part of the trough west slope; it is drawn on contact between sandy dolomites or dolomitic sandstones and a horizon of conspicuous gray, mixed grained sandstones and gravelstones, crossbedded, with a composition transitional from the Choruod to Kebekta. The transition horizon varies in thickness from 10 to 40 m. In the south and west of the trough, the base of the Kebekta suite contains basal conglomerates resting on the Archean basement in the west, and erosionally on rocks of the Choruod suite in the south. In the section we have studied (west and east slopes of the Ugui trough), visible thickness of the Kebekta suite is 100-720 m, depending on the depth of erosion. According to A. F. Petrov [11] and G. V. Biryulkin [1], its thickness may attain 1100-1700 m. The suite exhibits a poorly expressed cyclicity, with the cycles 100-200 m thick.

THE LITHOLOGY

It is clear from our description that Lower Proterozoic deposits of the Ugui trough are terrigenous, volcanic-sedimentary, and carbonate. However, the content of various rocks in the section is quite different. Sandstones account for at least 75-85% of the section. The figure for dolomites, the second most common rocks, is 5-11%; it is 1.5-8.0% for tuffites and tuffaceous siltstones of the Tuostai suite. The content of silty-argillaceous and psephitic rocks is relatively low: 2-4 and 3.5-7.0%, respectively.

The sandstones exhibit a progressive change in composition going up the section. Each suite is marked by a type of sandstone of its own, differing by mineral composition and structure. There are two such types in the Tuostai suite: clastic chert-quartz and arkosic

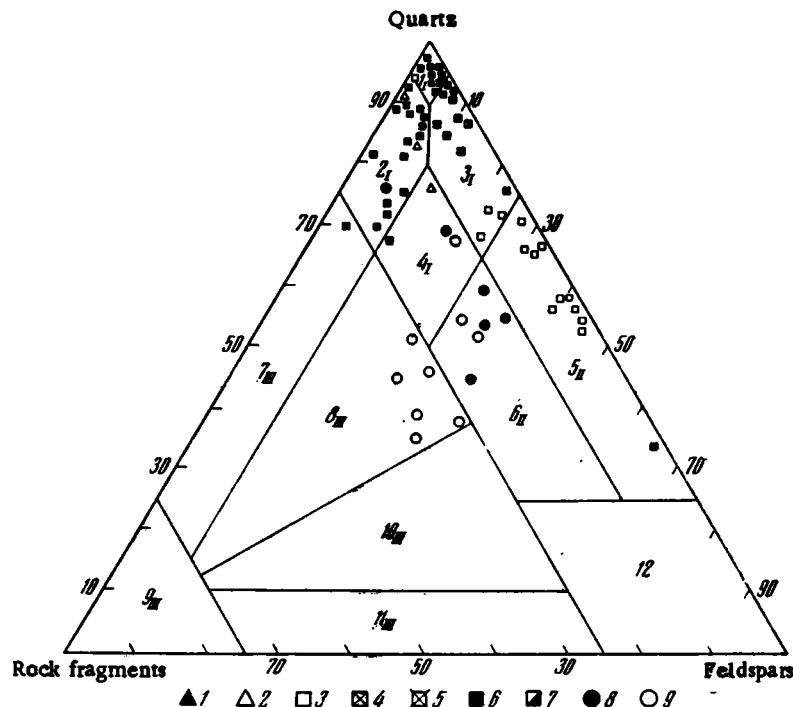


Fig. 3. Relationship between clastic components of sandstones from the Tuostai, Choruod, and Kebekta suites in classification triangle of V. D. Shutov [25] 1) tuffites and tuffaceous siltstones of the tuostai suite; 2) 1st horizon sandstones of the Tuostai suite; 3) same, 2nd horizon; 4) 1st horizon sandstones of the Choruod suite; 5) argillites and sandstones of the same horizon; 6) 2nd horizon, Choruod suite; 7) sandy dolomites and dolomitic sandstone of the same horizon; 8) sandstones of transition horizon, Kebekta suite; 9) sandstones of the Kebekta suite proper.

(Fig. 3). Sandstones of the first type have well rounded grains; they are relatively mature both structurally and mineralogically, in the absence of a pyroclastic admixture. More commonly such an admixture is present, and the rocks become transitional to tuffaceous siltstones. In that event, they exhibit two well-expressed granulometric fractions: the psammitic fraction is represented by rounded quartz grains; the silt fraction — by angular chips of volcanic glass, quartz, and feldspars.

The arkosic sandstones make up the second horizon of the Tuostai suite. The absence or low amount of cementing material leads to a strong development of regeneration, incorporation, and conforming structures responsible for a high density of the rocks. Granulometric composition of the sandstones exhibits the same two-fraction tendency: the silt fraction is represented by angular grains; the psammitic — by the rounded.

The Choruod sandstones differ from those of the underlying Tuostai and the overlying Kebekta suites by their peculiar composition, structure, and coloring. Predominant among them are gray, structurally and mineralogically highly mature varieties grouped in the three upper fields of Shutov's classification triangle (Fig. 3). Sandstones of the second Choruod horizon are mineralogically and structurally the most mature, monomineral quartz- and clastic chert-quartz in composition, highly rinsed from the pelitic addition. The interstitial chlorite-hydromica substance seldom exceeds 6%. Clastic material in most of them is well sorted (sorting factor, 1.5), with a majority of grains measuring 0.25-1.00 mm. The original outlines of the clastic grains, guessed at beneath the regeneration borders, indicate a high degree of sorting. These features of structural maturity determined a high initial porosity of the sandstones, subsequently obliterated by the epigenetic processes. It has been preserved in a portion of sandstones whose pores are filled up with a relict, metamorphosed bitumen accounting for 5-7% of area of the petrographic thin section.

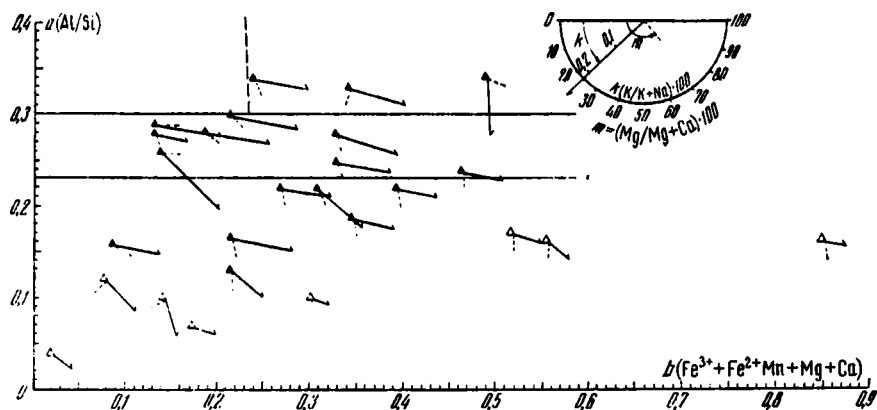


Fig. 4. Petrochemical parameters of rocks from the first Tuostai horizon. For symbols see Fig. 3.

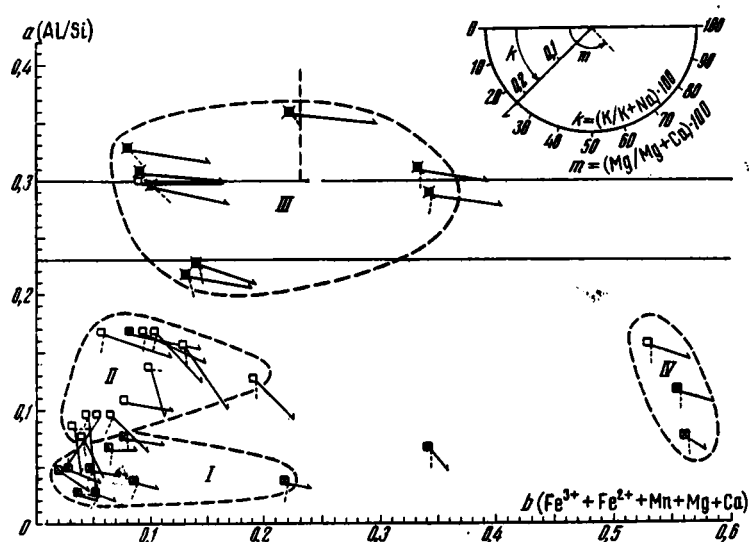


Fig. 5. Petrochemical parameters of the second Tuostai horizon and first Choruod horizon. For symbols see Fig. 3.

The Choruod sandstones contain dolomitic and dolomite-free varieties. The first is dominant in upper part of the horizon with 50% dolomite. The dolomite-free sandstones have a conform-regeneration structure.

I. M. Simanovch [18], a student of transformation for quartz and structure of the Choruod sandstones, believes that their postsedimentation alterations attained the stage of deep epigenesis resulting in a widespread development of dissolution structures under pressure; and also in quartz regeneration.

Sandstones of the Kebekta suite make up the next, peculiar group of terrigenous rocks differing from the underlying by composition and structure. Except for a thin transition horizon, these are red formations with a rock fragment content of 4-33% (Fig. 3). The most abundant are fragments of micro- to cryptogranular siliceous and felsitic rocks. Also present are fragments of microquartzites, porphyries, granite-gneisses, mica-quartz schists, orthophyres, granites, quartz-siltstones, and tuffs. Quartz fragments account for 35-60% of the total rock; feldspars (acidic plagioclase and K-varieties), for 20-30%. Dolomite (3-13% in individual pores), chlorite-hydromicaceous substances (2-12%), and dispersed iron hydroxides are almost always present in the cement. Iron oxides occur also in clastic grains of hematite and magnetite, 1-2%.

Granulometric composition of Kebekta sandstones is fairly uniform: mainly fine-grained (0.1-0.35 mm) varieties and coarse-grained (0.04-0.12 mm) siltstones.

TABLE 1. Correlation of Lower Proterozoic Deposits in the Ugui Trough With the Udokan Complex, According to Different Authors

L. I. Salop [16, 17]		V. P. Rabotnov [13]	L. M. Reutov, V. V. Lyankh- nitskii [14]	A. F. Pet- rov, [11]	G. V. Biryulkin et al. [1]		Proposed cor- relation	
Kemen series	Naming	Kebekta	Kebekta	Kebekta	Kebekta series	Olonnokon	Kebekta	
	Upper Sakukan					Choruod		
	Middle Sakukan						Telfer	Tuostai
	Lower Sakukan							
Chinel series	Butun	Khanin	Khanin	Khanin	Choruoda series	Ammuna Pravdinsk -	Olongitit	
	Aleksan- drovsk	Namsala	Namsala	Namsala				
	Chitkanda	Charodokan	Charodokan					
	Inyr							
Kodar series	Ayan			Charodo- kan				
	Ikabii							
	Boruryakh							
	Ortouryakh							
	Sygykta							
					Salata series	Tuostai		
						Olongitit		

In the classification triangle, sandstones of the Kebekta suite occupy fields of graywacke arkoses and arkosic graywackes (Fig. 3).

Thus, going up the section, composition of the arenaceous sediments progresses from quartz with an addition of pyroclastics, and arkosic in the lower red sequence (Tuostai suite), to feldspar-quartz, quartz clastic chert-quartz of the middle, gray sequence (Choruod suite), to graywackes of the upper red sequence (Kabekta suite).

Dolomites occur in the Olonga and Choruod suites of this section. According to G. V. Biryulkin et al. [1], they account for about 90% of the Olonga section and are represented by massive, thick-tabular, cherty dolomites, pink, reddish, to bordeaux-colored. The bordeaux and pink, jasperlike cherts occur in lenses and beds, 2-5 m thick. Under the microscope, the dolomites are fine-grained with numerous recrystallized pockets. The recrystallization fabric is mottled, lacy, venate, and massive. The cherty inclusions are microgranoblastic.

The Choruod dolomites, concentrated in the first and third horizons, are extremely inconsistent with respect to facies. These are light- to pink-gray to dark-colored rocks, sandy, thin-bedded with a pelitomorphous, fine- to medium-grained textures. Their distinctive feature is consistent evidence of erosion, expressed in intraformation breccias. This is most common in sandy dolomites of the third horizon, most often brecciated. The breccia fragments contain isolated varieties with a stromatolitic and microphytolitic structures. Another feature of the third horizon dolomites is silicification and a higher content of organic carbon.

Present in both the first and the third horizons are thin beds of microphytolitic dolomites with a well preserved interior structure of the microphytolites.

Tuffites and tuffaceous siltstones are typical rocks of the first Tuostai horizon, overlooked and unstudied. They are present in all the sections investigated and evidently are developed on this stratigraphic level over the entire Uguí trough. That makes them a good stratigraphic marker. At the same time, their identification suggests a volcanic activity

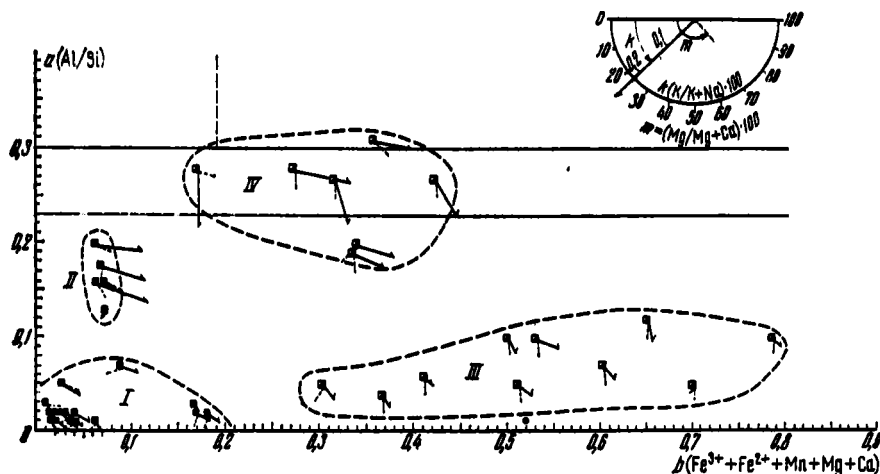


Fig. 6. Petrochemical parameters of rocks from the second and third Choruod horizons. For symbols see Fig. 3.

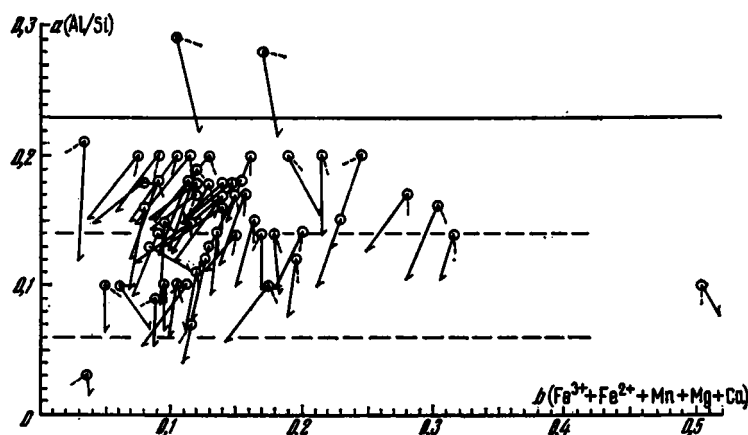


Fig. 7. Petrochemical parameters of rocks of the Kebekta suite. For symbols see Fig. 3.

in sources of the sedimentary material, so that certain geologic phenomena of the region, reflected in the composition and structure of the sedimentary rocks could be considered in that light.

Externally, tuffites and tuffaceous siltstones of the Tuostai suite are brown-cherry colored, silty rocks with a rough shearing surface and irregularly lenticular structure brought about by lenticular, sandy stringers. Other features, visible by the naked eye, are oval, yellow spots on the shearing surfaces, the result of iron oxides' reduction; and also white inclusions, isometric (1-6 mm) to lenticular (up to 7 mm long), of obviously crystalline dolomite.

A characteristic microstructural feature of the tuffites and tuffaceous siltstones is a well-expressed inhomogeneity of granulometric composition, with two fractions of the clastic grains differing by composition, size, and degree of rounding. Preponderance of this or that fraction in the stringers and lenses determines the thin-lenticular texture of the tuffites and tuffaceous siltstones. Frequency curves of their granulometric composition are typical two-maxima. The predominant is the silt fraction (60-80%) consisting of unrounded fragments of volcanic glass, quartz, and feldspars; 40-60% of silt material in thin sections is altered volcanic glass. The volcanic glass fragments are irregularly conchoidal, splintery, furcate, usually elongate, with the thickness/length ratio from 1/3 to 1/10. The glass is completely altered by secondary processes, devitrified, replaced by very fine-scale mica, chlorite, and dolomite, while maintaining the original outline of the fragments. The quartz fragments are sharp, angular, often with sorbed edges. The feldspar fragments, too, are altered to a considerable extent, replaced by dolomite and sericite. The unaltered varieties are mainly K-feldspars.

Quantitatively subordinate is the fraction of a normal clastic origin. It differs greatly from the pyroclastic fraction by composition and form of the grains: mainly rounded and semirounded quartz grains with a small amount of feldspars, mainly from the potassium group. The quartz grains are corroded at contact with the carbonate and ferruginous cement. The clastic grains vary in diameter from 0.06 to 0.30 mm.

The tuffites and tuffaceous siltstones are cemented with an argillaceous ferruginous substance: a yellowish-red aggregate with hematite incrustations, as seen in thin sections under reflected light. Isolated pockets and stringers often are cemented with dolomite and very fine-scale chlorites and hydromica.

PETROCHEMISTRY OF THE ROCKS

Petrochemical features of the terrigenous deposits were correlated on the basis of A. N. Neelov's petrographic classification of sedimentary rocks [9]. It is based on analysis of petrographic parameters calculated in atomic quantities or their ratios. The principal atomic parameters are used for the classification diagram: $\alpha = \text{Al}_2\text{O}_3/\text{SiO}_2$; $b = \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MnO} + \text{MgO} + \text{CaO}$; $n = \text{K}_2\text{O} + \text{Na}_2\text{O}$; $k = \text{K}_2\text{O}/(\text{K}_2\text{O} + \text{Na}_2\text{O})$; and $m = \text{MgO}/(\text{MgO} + \text{CaO})$.

Rocks of the Tuostai suite are marked by a high degree of petrochemical differentiation of their sedimentary material by parameters α and b (Fig. 4). Their alumina modulus α varies from 0.08 to 0.19. Such a broad range of the composition of rock specimens is accounted for by a great diversity of their clastic material consisting of two genetically different fractions — terrigenous and pyroclastic — mixed in inconsistent proportions; and also by fluctuations in the content of iron oxides and carbonates.

The high potassium content is the most typical feature of the tuffites and tuffaceous siltstones. At a moderate general alkalinity, $m = 0.1-0.2$, potassium modulus $k = 0.90-0.96$ in 80% of specimens analyzed, which relegates them to the superpotassic group. The remaining specimens belong to the high-potassium and sodium-potassium families.

The sedimentary-volcanic rocks, represented by silty tuffites, occupy in the classification triangle the field with $\alpha > 0.23$: basic tuffites. Their mean petrochemical formula is

$$S_{0.488}; b_{0.270}; m_{0.710}; f_{0.380}; a_{0.793}; t_{0.031}; n_{0.182}; k_{0.880}. \quad (1)$$

In the Neelov's petrochemical classification of volcanic products, alkalic K-basalts have parameters the closest to these.

The degree of chemical differentiation of rocks from the second Tuostai horizon is low because mineral composition of its sandstones is stable, corresponding to the arkoses. In addition, granulometric differentiation of sedimentary material from this subdivision also is low in the absence of siltstones and argillites. Consequently, parameter α fluctuates within a narrow range of 0.08-0.17. The low value of parameter $b = 0.03-0.19$ is the effect of a low iron and carbonate content (Fig. 5, field II).

In sandstones from the second horizon, parameter m varies from 0.10 to 0.17, marking them as moderately alkalic rocks. Their potassium content is appreciably higher than in the underlying tuffites. In the overwhelming majority of specimens, parameter k varies from 0.52 to 0.90, relegating them to families of Na-K, potassic, and high-potassium rocks.

Sedimentary formations of the first Choruod horizon are marked by a high degree of petrochemical differentiation, as clearly illustrated in diagram αb (Fig. 5), where sedimentary rocks of this horizon make up three well-defined fields (I, III, IV). Field I corresponds to monomictic quartz sandstones and their oligomictic feldspar-quartz varieties, more or less carbonate; field III — to polymictic siltstones and silty, pelitic argillites; and field IV — to sandy dolomites. As seen in diagram αb , sandstones of first horizon differ from the underlying Tuostai arkoses by lower values of parameter α , i.e., by a higher mineral maturity, low general alkalinity (parameter m seldom exceeding 0.06-0.07), and higher relative potassium content (0.80-0.95).

The siltstones and silty-pelitic argillites have higher values of parameter $\alpha = 2.2-3.6$. Judging from parameters m and k , these are moderately alkalic ($m = 0.16-0.19$), super-potassic ($k = 0.90-0.96$) rocks.

The considerable dispersion of parameter b is the effect of fluctuations of the dolomitic component — all the way from slightly dolomitic silty-sandy rocks and argillites to sandy dolomites and marls.

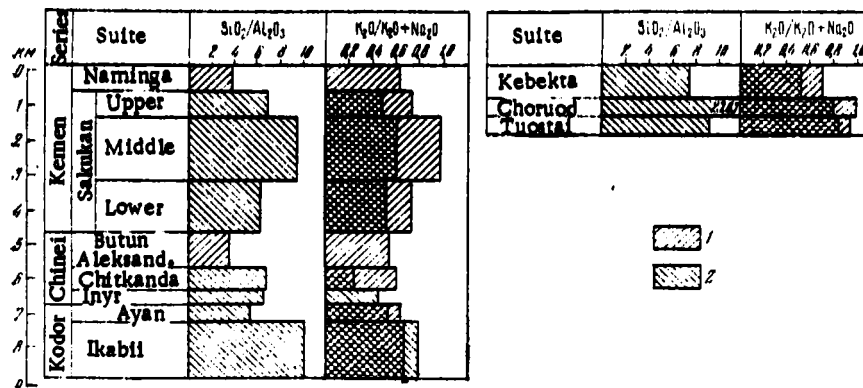


Fig. 8. Correlation of Lower Proterozoic sections in the Udokan and Ugui troughs by their thickness and petrochemical parameters: Hatching: 1) argillite, metargillites; 2) sandstones.

The petrochemical classification triangle for the second and third Choruod horizons (Fig. 6) quite definitely indicates four fields: field I corresponds to monomictic quartz sandstones (preponderantly rocks of the second Choruod horizon); field II, arkosic sandstones present in some of the sections; field III combines all the varieties of dolomites from clastic, sandy, and cherty to the microphytolitic and pelitomorphous. The diagram shows their greatly variable carbonate content. Finally, field IV characterizes the chemical composition of sandy argillites, marls, and siltstones present in the third Choruod horizon.

The Choruod sandstones are marked by lowest values of parameter α for section. For monomictic sandstones of the first horizon, $\alpha = 0.01-0.02$, seldom 0.07. For arkosic sandstones, not present in all the sections, $\alpha = 0.13-0.20$; the figure for the sandy argillites and marls is 0.19-0.31.

Strong differentiation by parameter b indicates changes in carbonate content in rocks of this suite from carbonate-free sandstones to almost pure dolomites.

The total alkalinity, very low (0.02-0.06) in the monomictic quartz sandstones (class of low-alkalinity rocks) rises to 0.10-0.15 in the arkoses and argillites (moderately alkaline rocks). However, the relative alkalinity remains as high as for the Tuostai suite (family of potassium and high-potassium rocks).

Disposition of representative points and vectors of petrographic parameters for rocks from the Kebekta suite fully corresponds to that observed in thin sections. The degree of sedimentary material differentiation by parameters α and b is rather low as compared with subdivisions described above (Fig. 7). That indicates a small array of rock types of this suite. The majority of the representative points concentrate in fields of polymictic and graywacke sandstones. Rocks of the Kebekta suite are superior in total alkalinity to those of the underlying Choruod deposits and belong to the moderately alkaline group (0.10-0.21). The greatest difference between the Kebekta sediments and all others of the section is with reference to parameter k . While rocks of the Tuostai and Choruod suites correspond to the potassic (0.60-0.75) and high potassium (0.75-0.90) families, those of the Kebekta suite are relatively low in potassium and belong to K-Na (0.20-0.41) and Na-K (0.41-0.60) families.

CORRELATION OF DEPOSITS IN THE UDOKAN AND UGUI TROUGHS

All the students of cupriferous sandstone deposits in the Ugui trough correlate them — stratigraphically, formationwise, and genetically — with the generally familiar deposits in the Udokan trough. The basis for such correlation is the geographic proximity and similar tectonics of these structures.

L. I. Salop [16, 17], who identified Lower Proterozoic deposits of Udokan as the Udokan series, differentiated them into three subseries: Kodar, Chinei, and Kemen. The Kodar subseries of the Udokan Range area consists of the Ikabii and Ayan suites. The Ikabii suite is made up of dark-colored, graphitic schists and phyllites with a horizon of white marbles; the Ayan suite is a rapid alternation of thin-bedded sandstones and siltstones. The Chinei subseries comprises the Inyr, Chitkanda, Aleksandrovsk, and Butun suites. The Inyr suite consists of thick-bedded sandstones; the Chitkanda — of sandstones with beds of schists and

quartzites; the Aleksandrovsk is an alternation of thin, carbonate rocks; and the Butun consists of siltstones and fine-grained sandstones with 1-2 m thick horizons of dolomites. The Kemen subseries consists of two suites: Sakukan sandstones with beds of siltstones, argillites, and gravelstones; and Naming siltstone with subordinate beds of phyllites and sandstones. According to Salop, the Udokan series is 13,000 m thick, on the average.

In identifying, after V. S. Fedorovskii [25], the Lower Proterozoic cupriferous schist-terrigenous sequences as the Udokan complex, Yu. V. Bogdanov et al. [4] doubt the existence of the Ikabii suite and the Kodar series as a whole as a stratigraphic unit of the Udokan subzone. They propose instead a bipartite structure of the Udokan complex as a component of the Chinei and Kemen series. According to L. V. Travin and V. P. Feoktistov [23], the base of the Kemen series includes the Talakan suite corresponding, according to L. I. Salop, to the Lower Sakukan suite. The Chinei flysch and the Kemen molasse series are, correspondingly, 3000 and 4000 m thick.

A correct correlation of cupriferous deposits in the Ugui and Udokan troughs is important on principle in paleotectonic reconstructions, correlation of ore-bearing levels, and determination of paleogeography and paleofacies responsible for development of Precambrian cupriferous sequences. As such, it is closely associated with prognostication of ore potential of the Udokan complex. At present, there is no unity of opinion on correlation of Proterozoic structures of these structures. The current correlation tables are based on lithological similarity of geological subdivisions correlated. As shown in the composite correlation Table 1, all the investigators agree on correlation of the Sakukan and the Kebekta suites. As for the lower part of the section, there is a considerable disagreement. A. F. Petrov, V. T. Rabotnov, and L. M. Reutov et al., correlate sub-Kebekta deposits of the Ugui trough with suites of the Chinei series, while Biryulkin et al. regards the lower part of the Ugui section as contemporaneous with lower part of the Kodar series, Udokan complex.

At the same time, there is conspicuous dissimilarity in the thickness of Proterozoic sections in question. Total thickness of the Udokan complex, 7000-13,000 m, is 5-10 times greater than total thickness of all the suites in the Ugui trough, 1300-2000 m.

Investigation shows that the main source of Lower Proterozoic sediments in the Ugui trough was west of it, at the site of the Archean Chara Block as understood by L. I. Salop. According to the majority of the investigators, the same regions were the main source of clastic material in the Udokan complex in the trough of the same name. N. N. Bakun has demonstrated that by mass measuring of the cross-bedding [6].

In our opinion, another source of sediments, quite important in the Tuostai time, was volcanic centers that produced fine potassic pyroclastic material. Even though their exact position is unknown, their effect, owing to an extensive area of their dispersion, must have been reflected in sediments of both troughs.

Thus, contemporaneous deposits of the Ugui and Udokan paleosedimentation basins came in from one and the same source, which certainly must have been reflected in their composition. We know that "the composition of sedimentary formations is determined by interaction or a combined effect of the climate and relief of the source area, and also of abrasion and sorting, on the weathering products" [12, p. 617]. Consequently, terrigenous sediments from one and the same region of Archean rocks with platform tectonics — such as the Chara Block — must have a similar petrochemical background and mineralogical maturity.

As a consequence, the general trend of the principal petrochemical parameters $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/(\text{K}_2\text{O} + \text{Na}_2\text{O})$ in sandstones from Lower Proterozoic sections in the Udokan and Ugui troughs must be the same.

Another marker in correlating sections of these structures is the stratigraphic level of deposits contaminated with high-potassium pyroclastic products. In sections we correlate, this level must have a higher $\text{K}_2\text{O}/(\text{K}_2\text{O} + \text{Na}_2\text{O})$ in sediments with a silt and pelitic grain size.

In Fig. 8, thickness of each suite of the Udokan and Ugui troughs is plotted on the vertical axis, on the corresponding scale; average silica-aluminum ratios for the sandstones, and potassium modulus for the sandstones and metargillites — on the horizontal axis.* The

*Moduli for the Udokan trough are calculated from average chemical composition for each suite cited by A. V. Sochava [21]. Mean chemical composition of rocks from the Ugui trough is given in Table 2.

TABLE 2. Mean Chemical Composition of Lower Proterozoic Rocks in the Ugui Trough, %

Suite	Horizon	Rock	Number of anal- yses	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Calcin- loss	P ₂ O ₅	Total
Kebekta	—	Sandstones Argillites	132 4	74,80 60,38	0,35 0,61	10,07 15,19	1,94 3,52	1,36 2,22	0,06 0,09	1,47 2,98	2,37 3,19	2,72 1,89	2,60 4,32	2,78 5,72	0,05 0,09	100,57 100,20
Choruod	Third	Sandstones Dolomites (brecciated, sandy, chert)	32 30	74,68 51,34	0,33 0,19	9,66 4,85	1,75 1,54	1,67 0,99	0,05 0,14	1,49 8,04	2,59 12,08	2,06 0,71	3,12 1,65	2,66 18,15	0,07 0,13	100,13 99,81
	Second	Sandstones	30	90,58	0,06	2,79	0,59	1,05	0,03	0,74	1,11	0,38	1,25	1,19	0,03	99,8
	First	Dolomitic sand- stones	18 5	86,63 56,10	0,09 0,13	5,42 5,73	0,73 1,04	0,99 0,54	0,01 0,08	0,46 7,56	0,71 10,08	0,64 0,20	3,16 3,11	1,16 15,76	0,01 0,04	100,01 100,37
		Argillites and sandstones	7	59,25	0,53	15,16	2,27	1,59	0,01	2,97	3,41	0,207	7,57	7,20	0,071	100,24
Tuostai	Second	Sandstones and gravelstones	7	73,29	0,25	9,78	1,09	1,04	0,02	1,50	2,53	1,05	5,06	4,46	0,02	100,1
	First	Conglomerate breccias	2	43,58	0,08	6,07	1,28	0,40	0,05	10,89	13,75	0,30	3,63	19,94	0,02	99,99
		Sandstones and gravelstones	4	77,81	0,063	5,04	0,71	0,80	0,04	1,59	5,17	0,51	2,75	5,04	0,01	99,53
		Tuffites, tuffaceous siltstones, and tuf- faceous sandstones	17	62,17	0,49	11,66	4,41	0,73	0,07	3,90	3,63	0,48	6,22	6,06	0,06	99,88
Olonglit	—	Cherty dolomites	7	17,80	He o6n.	0,33	0,09	0,06	0,06	18,35	24,03	0,10	0,35	38,01	0,07	99,25

frequency curve so obtained makes it possible to correlate the sections in question by their thickness and chemical composition. The entire Lower Proterozoic section of the Ugui trough (Fig. 8), beginning with the Tuostai suite, can be correlated with the Kemen series in Udokan. The entire lower part of the Udokan complex (Chinei and Kodar series) has a slightly different chemical composition of sediments. Its dominant rocks have a much lower silica/aluminum ratio and a substantially different ratio of the alkaline elements. Only the Kemen series contains the more mature Tuostai, Choruod, and Kebekta sandstones and a higher potassium content in rocks with a pelite-silt grain size from the Udokan complex.

The same holds true in comparing petrochemical diagrams for rocks in sections correlated. The petrochemical diagram for rocks of the Chitkanda and Alexandrovsk suites, Chinei series, cited by A. V. Sochava [20, 21] has no analogs among rocks in the Ugui trough. At the same time, petrochemical diagram for rocks from the Middle Sakukan subsuite [21] is close to those for the Tuostai and Choruod suites, differing from them by parameter b, owing to the high dolomite content in rocks of the Ugui trough (Figs. 4-6). Petrochemical parameters for rocks of the Upper Sakukan subsuite are identical with those for the Kebekta suite (Fig. 7).

Thus, there are no analogs of the Kodar and most of the Chinei series, Udokan complex, in the Lower Proterozoic section of the Ugui trough, so that sections of these troughs should be correlated beginning with the Lower Sakukan subsuite of the Kemen series or else with the Butun suite near top of the Chinei series, if the latter is taken as a stratigraphic analog of the Olongit suite.

This point is substantiated also by K-Ar determination of absolute age of high-potassium tuffites from the Tuostai suite, in the Laboratory of Geochronology and Isotope Geology, Institute of Geology, Yakutian Affiliate of Siberian Division, Academy of Sciences USSR, under N. I. Nenashev. As determined from ten analyses, this figure is 1704-1844 million years, not considering the two extreme figures, 1418 and 2214 million years. Considering the approximate character of these data, their similarity is obvious.

The use of absolute age determinations is based on two premises. First, development of pyroclastic material in the tuffites was contemporaneous, or nearly so, with sedimentation, so that absolute age determined on the pyroclastic material is the age of sedimentation. Second, the tuffite may contain normal sedimentary fragments of older rocks. Consequently, the absolute age may be older, but not younger.

Should the Tuostai suite be correlative with those of the Kodar series as the author of [2] has it, the age of its sediments must be 2400-2500 million years. If it is correlative with suites of the Chinei series, as the majority of other investigators have it, the Tuostai sediments again are older than 2000 million years. Our own data on absolute age of Tuostai tuffites, 1704-1844 million years are consistent with current views on age of the upper half of the Kemen series.

CONCLUSIONS

Analysis of thickness, chemical composition, and absolute age of the sediments unambiguously indicates that Lower Proterozoic deposits of the Ugui trough are contemporaneous solely with upper part of the Udokan complex: mainly sediments of the Kemen series, Udokan trough. The Lower Proterozoic section thickens up considerably south of the Ugui trough, in the direction of Udokan - in consequence of downward growth usual in transition from near-platform facies to miogeosynclinal.

LITERATURE CITED

1. G. V. Biryulkin, V. A. Kudryavtsev, and V. N. Salatkin, "Precambrian stratigraphy of the Ugui complex in western part of the Aldan Shield," in: *Precambrian Stratigraphy and Sedimentary Geology of the Far East* [in Russian], Izd. DVNTS AN SSSR, Vladivostok (1978), pp. 57-96.
2. G. V. Biryulkin, V. A. Kudryavtsev, and S. V. Nuzhnov, "Lower Proterozoic structures of the Aldan Shield," *Geol. Geofiz.*, No. 2, 16-25 (1983).
3. Yu. V. Bogdanov and V. P. Feoktistov, "Formation types of cupriferous sandstone deposits in Northern Trans-Baikal region," in: *Geology of Precambrian Mineral Deposits* [in Russian], Nauka, Leningrad (1981), pp. 147-154.
4. Yu. V. Bogdanov, O. P. Apolskii, and V. P. Feoktistov, "Petrochemistry and geochemistry of the Udokan complex, Northern Trans-Baikal region," *Litol. Polezn. Iskop.*, No. 5, 117-125 (1982).

5. M. Z. Glukhovskoi, "Some features of the tectonics of early development stages for the Olekma-Vitim mountain country," *Geotektonika*, No. 3, 35-59 (1969).
6. A. M. Leites, *The Lower Proterozoic of the Northwestern Olekma-Vitim Mountain Region* [in Russian], Nauka (1965).
7. Leites, A. M., M. V. Muratov, and V. S. Fedorovskii, "Paleoaulacogens and their place in development of the ancient platforms," *Dokl. AN SSSR*, 191, No. 6, 1366-1369 (1970).
8. K. B. Mokshantsev, "The tectonics of Yakutia," in: *Structure of the Crust and Distribution Pattern of Mineral Resources* [in Russian], Nauka (1969), pp. 5-42.
9. A. N. Neelov, *Petrochemical Classification of Metamorphic and Volcanic Rocks* [in Russian], Nauka (1980).
10. E. V. Pavlovskii, "Origin and development of the ancient platforms," in: *Problems of Comparative Tectonics of the Ancient Platforms* [in Russian], Nauka (1964), pp. 7-14.
11. A. F. Petrov, *Precambrian Orogenic Complex in the West of the Aldan Shield* [in Russian], Nauka, Novosibirsk (1976).
12. F. J. Pettijohn, *Sedimentary Rocks*, Harper and Row (1975).
13. V. T. Rabotnov, "Late Precambrian stratigraphy of the Olekma-Tokka watershed," *Dokl. Akad. Nauk SSSR*, 156, No. 6, 1351-1354 (1964).
14. L. M. Reutov and V. V. Lyakhnitskii, "Lower Proterozoic formations of the Olekma-Tokka watershed," in: *Materials on Geology and Mineral Resources of the Yakut ASSR*, No. 18, Yakutsk. Kn. Izd. (1968), pp. 93-104.
15. V. N. Salatkin, "Stratigraphy of the lower part of the Precambrian Udokan series, East Siberia," in: *News on the Geology of Yakutia*, No. 1, Yakutsk. Kn. Izd. (1971), pp. 17-22.
16. L. I. Salop, *Geology of the Baikal Mountain Region* [in Russian], Vol. 1, Nauka (1964).
17. L. I. Salop, *Geology of the Baikal Mountain Region* [in Russian], Vol. 2, Nauka (1967).
18. I. M. Simanovich, *Quartz in the Arenaceous Rocks* [in Russian], Nauka (1978).
19. S. S. Smelovskii, "Precambrian and Lower Paleozoic stratigraphy of Olekma-Vitim mountain region (north of the Chita area)," *Zap. Zabaikal. Fil. Geograf. Obshch. SSSR*, 81-227 (1966).
20. A. V. Sochava, *Precambrian and Phanerozoic Red Beds* [in Russian], Nauka (1979).
21. A. V. Sochava, "Lithology and petrochemistry of ore-bearing complexes in the Udokan deposit of cupriferous sandstones," in: *Geology of Precambrian Mineral Deposits* [in Russian], Nauka (1981), pp. 155-167.
22. Yu. A. Kosygin and L. M. Parfenov (eds.), *Tectonic Map of the Far East and Adjoining Areas* [in Russian], Izd. DVNTS AN SSSR (1978).
23. L. V. Travin and V. P. Feoktistov, "Stratigraphy of the Udokan series, Kodar-Udokan zone," *Tez. Dokl. I Nauchn. Konferentsii Geol. Sektsii im. V. A. Obrucheva*, 26-39 (1961).
24. V. S. Fedorovskii and A. M. Leites, "Geosynclinal troughs in Early Proterozoic of the Olekma-Vitim mountain region," *Geotektonika*, No. 4, 114-128 (1968).
25. V. S. Fedorovskii, *Lower Proterozoic Stratigraphy of the Kodar and Udokan Ranges* [in Russian], Nauka (1972).
26. V. D. Shutov, "Classification of terrigenous rocks and graywackes," in: *Graywackes* [in Russian], Nauka (1972), pp. 9-29.

A geological description is made of the Rogachevsk-Severotaininsk manganese-bearing province, which holds the highest commercial prospects in the Novaya Zemlya archipelago. Signs of carbonate and oxide-carbonate manganese ores are confined to Early Permian terrigenous rocks. Two types of rocks are distinguished: silicic-rhodochrositic and silicic-pyrolusite-rhodochrositic. A regional facies zonality of manganese ores is outlined. A hypothesis is proposed, postulating the basic ore-supplying function of the major Novaya Zemlya Fault. Various facts suggest the existence of a stratified polymetallic mineralization of Atasui type associated with the manganese metallization.

Brief information on the existence of manganese ore on Novaya Zemlya has been reported in earlier publications [1, 2].

The author presents a more comprehensive description of the manganese prospects of Rogachev-Severotaininsk province of Pai-Khoi-Novaya Zemlya archipelago; the province described in the paper is the most promising in that respect in this region (Fig. 1).

The geological structure of the province is determined by the Middle and Upper Paleozoic sedimentary volcanic-sedimentary formations (Fig. 2).

The oldest Devonian rocks are represented by all the three stages. Carbonate rocks, mainly limestone, dolomite, and clay limestone, are predominant among the Devonian. Besides carbonate rocks, there are argillite, siltstone, sandstone, basalt covers, and tuffs confined to the top of the Devonian. The overall thickness of the Devonian is approximately 2100 m.

The Carboniferous in the area is represented only by the lower stage, where two suites are distinguished. The lower suite (Rogachev C_{1rg}) displays mainly various silicic rocks: phthanites, silicites, jasperoids, and black carbonic argillites. In the upper suite (Minin C_{1ml}) light-gray solid limestones, sometimes intensely silicified at the top, are predominant. The Carboniferous beds are not thick, approximately 200-400 m. The Permian is most widespread, and presented by the lower and upper stages. The Lower Permian, and partially Upper Permian, have been described in this area as the Sokolov suite (P_{1-2sk}), with which all the known shows of carbonate and oxide-carbonate manganese ores are associated. The suite is characterized by a predominantly silicic-carbonate-silt-argillite composition, and occurs usually with stratigraphic disconformity on Lower Carboniferous rocks. At the base of the suite, no coarse-clastic rocks are present; the basal layers are limestone and clay schist. The upper boundary of the Sokolov suite is drawn by the appearance of thick members of gray polymict sandstone, typical for the Late Permian Belushian suite (P_{2bl}).

The Sokolov suite is subdivided into three subsuites; the middle one is manganese-bearing.

The lower subsuite consists of rhythmically interstratified gray pelitomorphic limestones, black silicic argillites, and silicites, and is consistent in composition throughout the occurrence area. Scarce nodules (up to 5 cm) of phosphorite, containing up to 30% of P₂O₅, are found in the argillite layers with a thickness of up to 25 m.

The middle subsuite consists of black argillite and silty argillite interstratified with silicic-rhodochrositic, and in some cases, pyrolusite-silicic-rhodochrositic ores.

All-Union Geological Scientific-Research Institute, Leningrad. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 59-69, May-June, 1986. Original article submitted July 11, 1984.

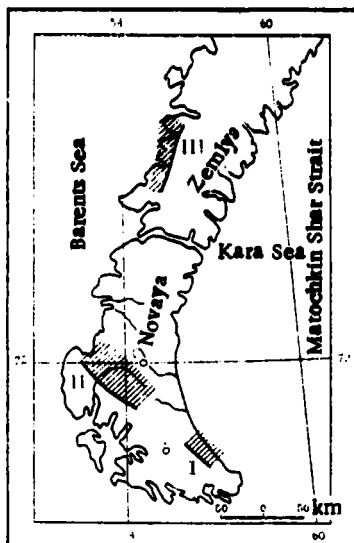


Fig. 1

Fig. 1. Manganese provinces in Novaya Zemlya (I — Kolodkin, II — Rogachev-Severotaininsk, III — Sul'menev).

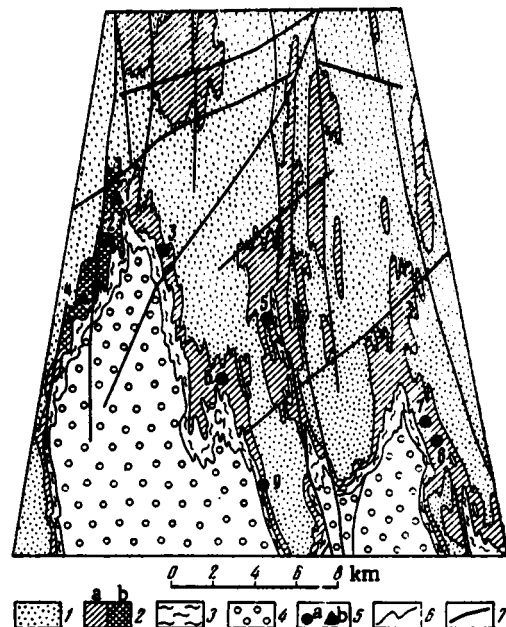


Fig. 2

Fig. 2. Geological map of Rogachev-Severotaininsk region (schematic): 1) Belusha suite P_{2bl} (sandstone, argillite); 2) Sokolov suite P_{1-2sk} (argillite silty argillite) with substantial presence of silicic-rhodochrosite ore (a) and silicic-pyrolusite-rhodochrosite ore (b); 3) Milin C_{1ml} and Rogachev C_{1rg} suites (limestone, argillite, phthanite); 4) Vadegi, Tainisk, Raisk suites D_3 (clayey limestone, limestone, sandstone, tuff, basalt); 5) signs of manganese ores, mainly of silicic-rhodochrosite (a) and silicic-pyrolusite-rhodochrosite (b) composition (1 — Severnoye, 2 — Blizhneye, 3 — Leningradskoye, 4 — Yuzhnoye, 5 — North Rogachev, 6 — Rogachev, 7 — Solnechnoye, 8 — Severotaininsk, 9 — Milin); 6) geological boundaries; 7) tectonic faults.

This portion of the suite has the maximum variability in lithologic composition and thickness. The productive subsuite is discussed in detail below.

The top subsuite consists of monotonically interstratified black argillite and clay siltstone with rare interlayers of gray small-grained polymict sandstones and chlydolite.

The age of the lower subsuite has been determined as Asselian-Sakmarian, that of the middle subsuite as lower Artalian, and upper subsuite, upper Artalian and partly Ufian age [1].

As has been noted earlier, the middle (productive) subsuite has a distinct lithologic variability, most pronounced in the northwestern-southeastern direction (Fig. 3). Three zones with different lithologic compositions of the productive subsuite are identified in this direction.

ZONE I

Zone I is characterized by the following composite geological profile.

The lower subsuite, 40 m thick, consists of fine interstratified silicic argillite, phthanite, and rhodochrosite. Rhodochrosite interlayers are few, and account for about 5%. The ore interlayers are up to 10 cm thick. The middle productive subsuite is subdivided into four horizons.

Horizon 1 (bottom), up to 5 m thick, typically consists of a member of silty argillite with minor presence of rhodochrosite interlayers. The latter amounts to about 5%.

Horizon 2, up to 40 m thick, is characterized by an interstratification of green-gray argillite with rhodochrosite interlayers. Rhodochrosite interlayers amount up to 50%.

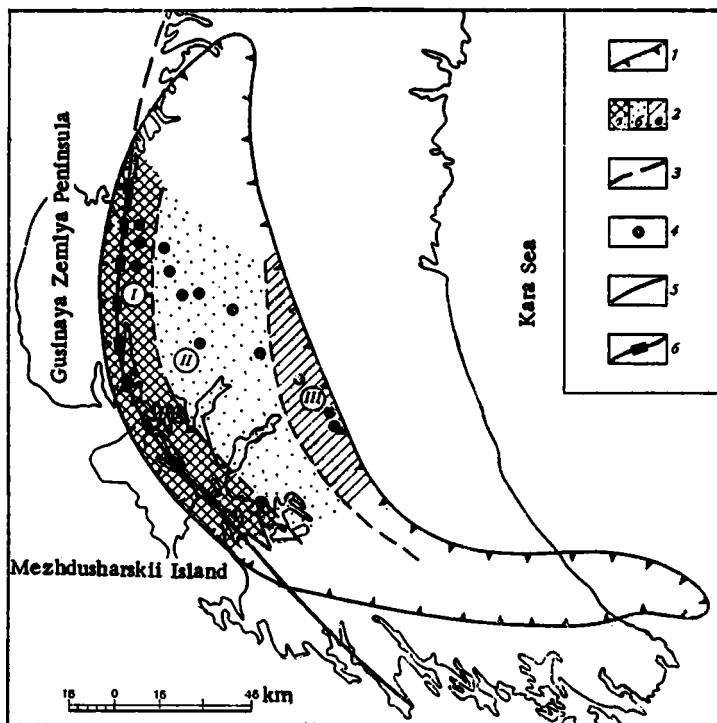


Fig. 3. Facies zones of the Lower Permian manganese mineralization of Rogachev-Severotainisk region and its flanks. 1) Outer Kara depression; 2) facies zones characterizing the accumulation of various ore types at the peak of hydrothermal activity (a - pyrolusite-silicic-rhodochrosite, b - silicic-rhodochrosite, c - silicic) and their numbers (I-III); 3) zone boundaries; 4) sites of profiles characterizing facies zones; 5) main Novaya Zemlya Fault; 6) Rogachev zone of main Novaya Zemlya Fault.

The rhodochrosite in this horizon contains spherulite insets and considerable chalcopryrite. Grains up to 2 mm across are found.

Horizon 3, 40 m thick, consists of interstratified black shelly, sandy argillite, up to 5 m thick, with finely interstratified members of black argillite and rhodochrosite, with dispersed pyrolusite insets confined to layers. The number of metalliferous interlayers in the members amounts to up to 80%. The number of metalliferous members is 3-4, with a total thickness of up to 30 m.

Horizon 4, about 40 m thick, is similar in composition to horizon 2; it consists of interstratified silty argillite and rhodochrosite. Rhodochrosite interlayers amount up to 40% of the total number of layers.

The overall thickness of the productive subsuite is 125 m.

The top subsuite, 200 m thick, consists mainly of black foliated argillites, with rare interlayers of silty calcareous ore, with obliquely stratified argillites at the top.

The zone is about 15 km wide.

ZONE II

The rocks of the Sokolov suite of this zone are characterized by the following composite profile.

The lower subsuite, about 30 m thick, is subdivided into two horizons.

Horizon 1, on average 10 m thick, is predominantly of a clay-carbonate composition. It consists of interstratified black foliated argillites with up to 2 m thick interlayers of gray pelitomorphous and sandy, obliquely stratified limestones, which sometimes are crinoidal.

Horizon 2, up to 20 m thick, consists of interstratified black foliated silicic argillites with thin phthanite interlayers.

The middle subsuite is subdivided into four horizons.

Horizon 1, 20 m thick, consists of interstratified members of silty argillites, up to 10 m thick, and black foliated argillites, which often contain phosphorite nodules up to 5 cm in diameter. The number of phosphorite nodules is small; they account for about 3-5% of the material. Silty argillites sometimes contain interlayers of silicic rhodochrosites, which are thin (not more than 5-7 cm). The number of these layers is also small (~5%).

Horizon 2, 35 m thick, consists of interstratified silty green-gray argillites, with interlayers of silicic rhodochrosites, amounting up to 50% of the profile. The metalliferous interlayers are up to 10 cm thick.

Horizon 3, up to 50 m thick, consists of interstratified members of black, shelly, sandy argillites, up to 5-7 m thick, and members with fine alternation of argillites and rhodochrosites. The productive members are up to 12 m thick. The number of metalliferous members is up to three, with metalliferous interlayers' contents up to 80%.

Horizon 4, 45 m thick, consists of interstratified silty green-gray argillites with silicic rhodochrosites up to 10 cm. Metalliferous interlayers in the member amount to 30% of the total. The productive portion is 150 m thick.

The middle subsuite is overlain by a clay bed, 200 m thick, with interlayers of sandstones, chlydolites, and limestones. A presence of minor lenses of a carbonate composition has been recorded. The zone is 30 km wide.

ZONE III

The composite geological profile can be described as follows.

The lower suite, 15 m thick, consists of alternating gray pelitomorphous and crinoidal limestones with black foliated argillites interstratified with scarce phthanite interlayers.

The middle (productive) subsuite, 70 m thick, is divided into three horizons.

Horizon 1, 10 m thick, consists of interstratified silty silicified green-gray argillite and light-gray silicite. The silicite layers are up to 5-7 cm thick. Their number accounts for 50% of the units.

Horizon 2, 35 m thick, consists of interstratified members of black argillite and members with alternating argillite and silicic rhodochrosite, up to 7 cm thick. Metalliferous layers account for 30-40% of all units.

Horizon 3, 25 m thick, consists of interstratified silty silicified green-gray argillite and light-gray silicite. It is similar to the first horizon.

The top subsuite underlying the productive layer is 90 m thick, and consists mainly of black foliated and silty argillite, with sandstone and chlydolite interlayers up to 5 m thick. The zone is 15 km wide.

The analysis of the structure and composition of the productive subsuite of the Sokolov suite and its individual zones indicates a facies alteration in the northwest-southeast direction, with a transition of carbonaceous manganese ore to silicic-carbonate and silicite.

The author links this succession of facies with the zonal distribution of manganese, silica, and other elements from the main Novaya Zemlya Fault, which is assumed to be the main metalliferous source.

ORE COMPOSITION

Most of the reserves of manganese ores in Rogachev-Severotaininsk manganese province are silicic-rhodochrosite ores, with a minor proportion of silicic-pyrolusite-rhodochrosite ores.

The data on the composition of ores indicates a perfect analogy throughout the region, confirming that the basin is a consistent entity. At the same time, there are differences in the composition of the manganese ores in the northwest-southeast direction, determining the facies of metallization settings.

TABLE 1. Chemical Analyses of Manganese Ores from Rogachev-Severotainisk Region

Ore type	Specimen no.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	TiO ₂	P ₂ O ₅	Mn	MnO
Silicic-rhodochrosite	86-2	18,0	1,75	1,26	0,15	0,090	0,156	30,06	38,78
	91-2-144	34,5	2,65	1,43	1,00	0,100	0,117	20,86	27,09
	6478-146	46,8	7,30	1,35	3,15	0,420	0,103	10,47	13,51
Pyrolusite-silicic-rhodochrosite	87-1	30,8	4,30	2,55	0,29	0,150	0,186	20,23	21,09
	77-4	36,5	5,30	4,18	3,44	0,118	0,083	14,76	19,04
	82-3	32,8	5,45	3,15	3,14	0,120	1,625	15,23	19,65

Ore type	Specimen no.	MnO ₂	CaO	MgO	SO ₂	K ₂ O	Na ₂ O	Calcin. loss	Σ	H ₂ O
Silicic-rhodochrosite	86-2	None	6,4	2,50	0,118	0,45	0,20	30,57	100,4	30,32
	91-2-144	"	5,9	3,25	0,134	0,25	0,29	23,63	100,3	40,32
	6478-146	"	5,0	3,47	0,550	1,27	0,37	16,93	100,2	20,53
Pyrolusite-silicic-rhodochrosite	87-1	6,33	7,9	2,57	0,134	0,72	0,58	23,02	100,5	21,17
	77-4	None	5,7	4,17	0,212	0,24	0,24	21,29	100,5	10,54
	82-3	"	10,5	3,12	0,134	0,50	1,12	22,23	100,5	40,72

Silicic-rhodochrosite ore is widespread throughout the territory, while silicic ore is more common in the southeastern part.

The ore of this type is characterized by a high hardness factor, due to the high (up to 50% and more) silica content. The ores exhibit a broad spectrum of appearances; they vary from light gray to dark gray, and sometimes pink-brown coloring. The ores have an uneven, cavitated, broken surface. The ore structures vary, but mostly are massive, lumpy, lenticular, less often collomorphous-striated.

Silicic ores with lenticular and collomorphous structures occur mainly in the northwestern part of the province (ore shows at Severnoe and Blizhnyaya). Such structures are due mainly to rhodochrosite and silica differentiation in the ore. Lenticular and collomorphous insets are filled with silica, with a small rhodochrosite component (up to 5%), while the groundmass is rhodochrosite, with a minor silica admixture. In most silicic carbonaceous manganese ores with a massive ore variegated structure, the silica and rhodochrosite are distributed evenly.

On the weathering surface, silicic ore has an oxidized crustlet, up to 5 mm thick. Mineralographic investigation has determined dispersed pyrolusite and carbonaceous insets in the oxidized crustlet.

The silicic-rhodochrositic ores include the ore minerals: manganese carbonates — rhodochrosite, calcium rhodochrosite, and ferrorhodochrosite; manganese sulfide — alabandine; and also pyrite, sphalerite, and chalcopryrite; and nonore minerals — quartz, clay minerals, muscovite, and carbonic matter.

Phosphorite in small amounts is present as an impurity.

Manganese carbonates form the bulk of the carbonate and oxide-carbonate ores. Various minerals are distinguished: rhodochrosite (MnO 55, CaO 5, MgO 0.25%), calcium rhodochrosite or mangano-calcite (MnO 44, CaO 10, MgO 3%), and ferrorhodochrosite; rhodochrosite is most widespread. The presence of all the three minerals in the ores is confirmed by chemical, x-ray, structural, and thermal investigations.

Manganese carbonates are seen in polished sections as small-crystalline (<0.005 mm) aggregates, and microspherulitic (d 0.01 mm) and spherulitic (d 0.1–0.3 mm) units. The predominant texture is microcrystalline. Microspherulitic and spherulitic forms are much less frequent.

Manganese carbonates in a pure form are mostly white-gray and gray; the brownish-gray and brownish coloring indicates the presence of clay matter, manganese, and iron hydroxides, and dispersed pyrite insets.

Spherulitic units of manganese carbonates are of an earlier origin. Subsequently, they decayed, giving rise to small spherulites and microcrystalline aggregates, and retaining just relics of the original texture.

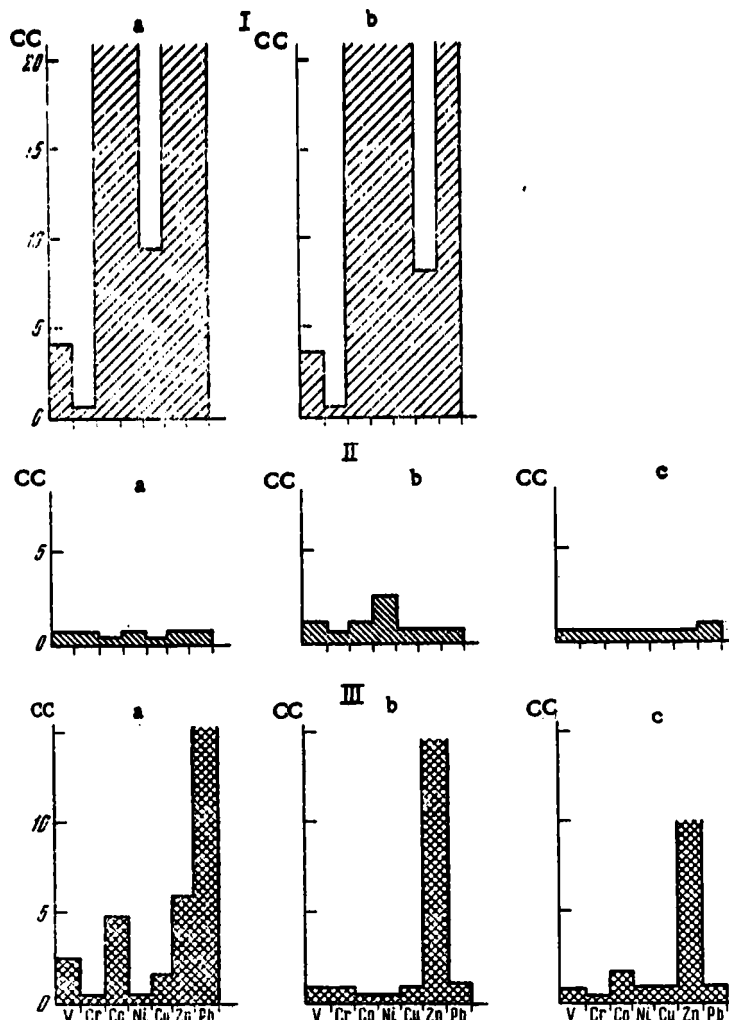


Fig. 4. Distribution of clarke concentrations (CC) of minor elements in manganese ores of various geneeses (after [9] and sampling of ore shows in Novaya Zemlya). I) Fe-Mn nodules (a - Pacific, b - Atlantic); II) sedimentary deposits (a - Nikopol, b - Chiatura); III) volcanogenic-sedimentary deposits (a - California, b - Karazhal, c - Novaya Zemlya).

During the ore oxidation, microspherulites and granular aggregates of manganese carbonates were replaced by manganese oxides and also manganese and iron hydroxides.

Spherulites are typically 0.3 mm across.

Dispersed pyrite and small quantities of sphalerite and chalcopyrite are seen regularly in the rocks. The ore shows at Blizhnii (northwestern part of the province) and Goluboi stream (center of the province) have sulfide manganese mineralization in the form of alabandine in silicic ore.

The highest level of sphalerite contamination in ore is observed in the lower part of the productive subsuite of the Sokolov suite, mainly in the northwestern part of the province (Blizhnyaya and Severnoe ore shows). Sphalerite is typically confined to lenticular and round units filled with microgranular quartz. Sphalerite grains are corroded, measuring up to 2 mm across.

Chalcopyrite occurs together with sphalerite, but less often. Grain sizes are up to 0.2 mm.

Silicic pyrolusite-rhodochrosite ore is found mainly in the northwestern part of the province (Blizhnyaya and Severnoe), although minor amounts have been found in the central part as well.

The ores of these types are of a lesser density than carbonate ores.

By appearance, they are diverse as well as carbonate ores; the pigmentation ranges from dark gray to black. Three ore structure types are distinguished: solid, striated, and collo-morphous-striated. The striation of the ores is due to the alternation of silicic carbonate interlayers and coalified clayey silicic-carbonate interlayers with dispersed pyrolusite inlets.

Pyrolusite aggregations sometimes form pseudo-oolites of a round shape, measuring up to 0.3 mm across, endowing the rock with a pseudo-oolitic texture. Most ores have a microlumpy texture. On the weathering surface, this ore (as well as carbonate ore) has an oxide crust-let. Oxide-carbonate ores have been studied in depth as well as on the surface. Specimens from the depths of 75-100 m (site 4) also exhibited ore with dispersed pyrolusite. These data could indicate a synergy of oxide manganese minerals.

Pyrolusite is found as needles up to 0.3 mm long, as well as in microgranular segregations. Silica, clay minerals, coaly matter, and pyrite are present as impurities. Impurity concentrations attain up to 40%.

No significant increase in the manganese content compared with carbonate rocks of silicic type is observed in oxide-carbonate ores; the manganese concentration is, on average, 20-30%.

During this study, the manganese (carbonate and oxidized) ores were analyzed for five main components: manganese, iron, silica, phosphorus, and sulfur. Complete chemical analyses of ore varieties were also performed; in addition, semiquantitative spectral analyses were made.

Table 1 gives the results of complete chemical analysis of the main types of manganese ores performed at the Central Laboratory of Yuzhukrgeologiya, Southern Geological Association. The chemical composition reveals a variegated picture of manganese content in various ore types. The semiquantitative spectral analysis of carbonate rocks indicated a heightened content of Zn, up to 1% (average 0.2-0.5%), Co (average 0.007%), Ba up to 1, and Cu up to 0.7%. A direct correlation of manganese and zinc has been established. The Zn, Cu, and Ba concentrations rise in the ores located in the north-northwestern part of the province.

An analysis of the distribution features of minor elements (V, Cr, Co, Ni, Cu, Zn, Pb) in Novaya Zemlya manganese ores and genetically cognate ores suggested that these are deposits with an endogenous source of manganese.

The manganese ore of Novaya Zemlya has mostly typical contents of minor elements, but a heightened content of Zn (concentration clark CC 10) and Co (CC 2-4). This distribution of minor elements in the manganese ore correlates well with the ores of the manganese deposits known to have an endogenous metalliferous influx (Fig. 4).

CONFINEMENT OF THE MANGANESE METALLIZATION TO MAIN NOVAYA ZEMLYA FAULT ZONE

The magmatic activity in the southern island of Novaya Zemlya is fairly widespread in space and time, and especially pronounced during the Late Devonian.

According to Timofeeva [7], the volcanic processes in the southern island of the Novaya Zemlya archipelago include explosions and effusions of basic rocks along the long-lived deep-lying faults. Kovaleva, Timofeev et al. [5] have identified three principal zones of longitudinal deep long-lived faults: Rogachev, Renek, and Kolodkin (see Fig. 3). The Rogachev zone is a part of the principle Novaya Zemlya Fault.

The Rogachev zone, 5-10 km wide, and about 200 km long, is traceable submeridionally from the Sakhanin Bay in the south to the mouth of Vadegi-l River in the north. On the surface, the zone is observed as a series of downthrows and upthrows. The amplitudes of vertical displacements are small, within the first tens of meters. At the beginning of the Late Devonian, the fault was a magma-conducting channel, and volcanic apparatus of this age have been identified within this zone. The typical magmatic formations in the Rogachev zone of the principal Novaya Zemlya Fault are volcanic products of a derivative tholeiitic magma, referred by Timofeeva [7] to the general Kostinsha magmatic complex.

Numerous instances of copper mineralization are associated with the volcanic rocks of the Kostinsha magmatic complex.

The Carboniferous and the Early Permian stages in the development of the southern island of Novaya Zemlya were associated with hydrothermal activity, expressed in the formation of numerous quartz and quartz-carbonate veins and veinlets, silicification, pyritization, sericitization, and partial albitization of rocks of various ages and compositions. The hydrothermal activity (as well as volcanic activity) is manifest in Rogachev zone of the principal Novaya Zemlya Fault. It is associated with various forms of ore mineralization: chalcopyrite, fluorite, etc.

On Mezhdusharsky Island, in the near-fault area of the Carboniferous and the Permian, a metallometric halo of copper is observed, measuring 25×2 km, and also confined to the zone of principal Novaya Zemlya Fault.

The hydrothermal activity of the Early Permian, best seen in Rogachev zone of the fault, is linked by the present author with the accumulation of manganese carbonate ores as well. These types of metallization have been described by Dzotsenidze [3], who gave numerous examples where ore did not form necessarily at the same time with submarine volcanic activity, but on the contrary, in conjunction with attenuating volcanic activity and increasing hydrothermal activity.

In considering again the facies zonality of the manganese-rich part of Sokolov suite, we see that the highest manganese, copper, and zinc concentrations are confined to zone I, and silica concentrations to zone III.

In view of different geochemical mobilities of manganese, copper, zinc, and silicon, Strakhov [8] noted that the least mobile copper, zinc, and manganese precipitated closer to mineralization-supply ducts of volcanogenic-sedimentary submerged manganese deposits. The most mobile silica is typically found at a greater distance from this source. High silica concentrations in the manganese ores and in their facies analogs should also, in the author's view, be connected with hydrothermal activity.

The formation of the Lower Permian in Novaya Zemlya, according to Ustritski [11], was confined to the central part of the immense Pai-Khoi-Novaya Zemlya trough that existed at that time.* In the north, the trough became narrower and less deep, and ended near Zhelaniye Cape, and in southwest was conjugated orthogonally with the Urals foredeep.

The trough apparently varied in depth, and appeared as a series of seafloor rises and depressions from Pai-Khoi to Zhelaniye Cape. The deepest parts of the trough were apparently the Sul'menev, Rogachev-Severotaininsk and Pai-Khoi manganese provinces. The Rogachev-Severotaininsk deposits were formed in the deepest environments.

The deep-water origin of these areas is confirmed by the following facts: the virtual absence of benthic fauna and carbonate sediment profile (small-size benthic forms), pyritization, the structures typical for roiling and rock downsides, etc. The peculiar stagnant depressions were apparently favorable structural-geochemical "traps" for manganese accumulation.

A unidirectional zonal distribution of manganese mineralization eastward from the principal Novaya Zemlya Fault is associated with the fact that this fault was situated on the western side of Pai-Khoi-Novaya Zemlya trough. The principal direction of the metalliferous solution flow would also be eastward, i.e., toward the middle of the trough.

The activity of the fault, determined by the influx of the manganese into the sedimentation basin, started at the time of formation of lower Sokolov subsuite sediments. This is indicated by low rhodochrosite contents in the lower subsuite of zone I.

Most active manganese influx associated with hydrothermal activity took place at the time of formation of the middle subsuite (ore horizon 3: the richest ore horizon, with fine interstratification of rhodochrosite and argillite). In addition, manganese mineralization at that time is most remote from Rogachev fault which, in this horizon, reaches to the third facies zone.

The appearance of the manganese in an oxide form in the first facies zone is apparently associated with the highest degree of water aeration, as compared with other facies zones. When the third ore horizon was formed, the hydrothermal activity, as has been mentioned, was

*Ustritskii [10] assumes that the Lower Permian of the Sokolov suite was formed in a deep-water ocean setting.

intense, which probably resulted in the highest degree of aeration of water. Part of manganese dissolved in water rose with water into the photosynthesis zone, where manganese could be absorbed by microorganisms, and, after their death, precipitated in an oxide form. It is possible that, in dissolved form, manganese with water reached the zone of an oxidative environment, and minor amounts of it precipitated in an oxide form.

In considering the zonal distribution of manganese and silica, in relation to the Novaya Zemlya Fault, we see that heightened copper and zinc contents are observed in the first facies zone (see Fig. 3). The highest prospects for this mineralization should be linked with the clay-silicic Early Permian sediments and Carboniferous carbonate sediments. Many of the polymetallic and copper deposits of volcanogenic-sedimentary type exhibit a characteristic lateral and vertical transition to iron-manganese metallization [6].

The possible occurrence of a polymetallic mineralization associated with Lower Carboniferous carbonates is also suggested by signs of fluoride mineralization in these sediments. It has been established [4] that most stratiform deposits of nonferrous metals of a volcanogenic-sedimentary genesis contain such "volcanogenic" elements as barium (in the form of barite) and fluorine (in the form of fluorite).

In addition to the hydrothermal-sedimentary manganese ores described in the article, the area contains a number of ore shows of high-grade oxidized manganese. The ores are confined to the zones of rupture dislocations crossing horizons with silicic-rhodochrosite ores. The zones are characterized by hydrothermal alteration, quartzification, and lixiviation. Some of the zones are up to 3000 m long and 100-200 m wide. The altered zones sometimes include lenses consisting of venous, brecciated, and solid vernadite-pyrolusite-psilomelane ores. Mn content in them is up to 33.26% (based on dredge sampling).

The Rogachev-Severotaininsk province of Novaya Zemlya is a new major manganese-rich Early Permian basin. Various types of manganese ores associated with characteristic facies zones have been described in this region.

The highest prospects for finding manganese deposits in the carbonate form are associated with the sediments of the first facies zone (see Fig. 3) nearest to the area of the principal Novaya Zemlya Fault.

Generally, in Novaya Zemlya, promising manganese provinces can be found in areas of pronounced magmatic activity followed by hydrothermal activity.

Manganese in oxide form is most likely to be found at sites of intensive water aeration, where it was accumulated in deep-sea conditions. In shallower facies, manganese can also be found, where hydrothermal activity was intensive.

Since the stratiform carbonate manganese ores of a hydrothermal-sedimentary genesis in Novaya Zemlya are similar to the manganese deposits of Atasui type, stratiform copper, lead, and zinc deposits are also likely to be found in Novaya Zemlya.

LITERATURE CITED

1. S. K. Voyakovskii, V. F. Il'in, L. G. Pavlov, et al., "Novaya Zemlya is a new manganese province," in: *Manganese Mineralization in the Territory of the USSR* [in Russian], Nauka, Moscow (1984), pp. 174-177.
2. S. K. Voyakovskii, V. F. Il'in, L. G. Pavlov, et al., "Stratiform manganese ore shows in Novaya Zemlya," in: *The Geology of the Southern Island of Novaya Zemlya* [in Russian], PGO Sevmorgeologiya, Leningrad (1982), pp. 121-124.
3. G. S. Dzotsenidze, *The Role of Volcanic Activity in the Formation of Sedimentary Rocks and Ores* [in Russian], Nedra, Moscow (1969).
4. A. M. Karpunin, *Stratiform Deposits of Nonferrous Metals* [in Russian], Nedra, Leningrad (1974).
5. G. N. Kovaleva, O. P. Timofeev, and G. V. Trifanov, "Folded structures of the southern island of Novaya Zemlya," in: *Geology of the Southern Island of Novaya Zemlya* [in Russian], PGO Sevmorgeologiya, Leningrad (1982), pp. 88-99.
6. E. I. Kutyrev, *Geology and Prediction of Conformable Copper, Lead, and Zinc Deposits* [in Russian], Nedra, Leningrad (1984).
7. T. N. Timofeev, "Middle and Late Devonian volcanism of the southern Novaya Zemlya," in: *The Geology of the Southern Island of Novaya Zemlya* [in Russian], PGO Sevmorgeologiya, Leningrad (1982), pp. 68-77.

8. N. M. Strakhov, "Studies of submarine volcanogenic-sedimentary rock formation," in: General Problems of Geology, Lithology, and Geochemistry [in Russian], Nauka, Moscow (1983), pp. 537-550.
9. N. M. Strakhov, E. S. Zalmanzon, I. V. Belova, et al., "Minor elements in sedimentary manganese metallization process," *Litol. Polezn. Iksop.*, No. 3, 3-33 (1967).
10. V. I. Ustritskii, "Correlations of the Urals, Pai-Khoy, Novaya Zemlya, and Taimyr," *Geotektonika*, No. 1, 51-61 (1985).
11. V. I. Ustritskii, "The Permian stage in the development of Novaya Zemlya," in: The Tectonics of the Arctic Region: Folded Basement of Shelf Sedimentation Basins [in Russian], NIIGA, Leningrad (1980), pp. 41-54.

APATITIC SANDSTONES IN THE HEADWATERS OF THE SELIGDAR RIVER,
SOUTH YAKUTIA (ALDAN CRYSTALLINE SHIELD)

A. G. Bulakh and V. N. Shvanov

UDC 552.51:549.753.1 (571.5)

Apatitic sandstones in the Seligdar apatite region, associated with the Precambrian Iengr series, and apatitic sandstones and grits of the overlying Lower Cambrian Yudom suite, are described. It is shown that the apatite is clastic in origin and, together with quartz and feldspar, forms apatite-bearing quartz-feldspar sandstones or grits. The source of the clastic apatite is the Seligdar apatite deposit.

Apatitic sandstones are known to be extremely rare. Therefore, the discovery of sandstones in the headwaters (source area) of the Seligdar River with 60% or more apatite fragments, xenocrysts, and even pebbles, is of considerable interest. Furthermore, they serve as a basis for evaluating several hypotheses for the origin of the Seligdar apatites. These sandstones have been reported in [3, 5, 6], but their composition and geological associations have not been satisfactorily described.

The Seligdar apatite deposit, in the Seligdar headwaters, is located in interbedded schists, gneisses, and carbonate rocks of the Iengr series. Various descriptions of the deposit and its structure have been presented in [3-5, 6, 7]. The views of one of the present authors, based on a study of the mineralogy and petrology of the rocks and ores and their structural relationships, as revealed by exploratory drilling, have been published before [1, 2].

The ore region has a distinct two-story structure (Fig. 1). The lower level, containing the ore, is composed of various schists and gneisses with beds of diopside, phlogopite-diopside, and magnetite-phlogopite-forsterite rocks, marble, and calciphyre. Most of the ore is associated with apatite-hematite-carbonate rocks. The upper level is made up of transgressive platformal deposits of the Lower Cambrian Yudom suite, the lower part of which is breccia formed from underlying rocks, grit, sandstone, and sandy dolomite, grading upward into dolomite with sandy dolomite and limestone interbeds. Carbonate rocks of the Yudom suite are intruded by Mesozoic syenite porphyry sills.

The characteristic feature of the ore region is widely developed tectonic faulting which has resulted in vertical displacement of large and small blocks (Fig. 2), brecciation, mylonitization, dike swarms, and other features. The block faulting took place in several stages: pre-Yudom and post-Yudom, and post-Mesozoic movements have been clearly established [1]. A block-fault interpretation of the structure of the ore deposit has also been presented in [4].

Apatitic and apatite-bearing sandstones were found in the early years (1973-1975) of study of the deposit by Tungusov, Galkin, Dobrynin, Priemov, and Fedchenko. According to the concept at that time, the sandstones appeared to be horizontal intercalations and lenses

Leningrad State University. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 70-77, May-June, 1986. Original article submitted June 1, 1984.

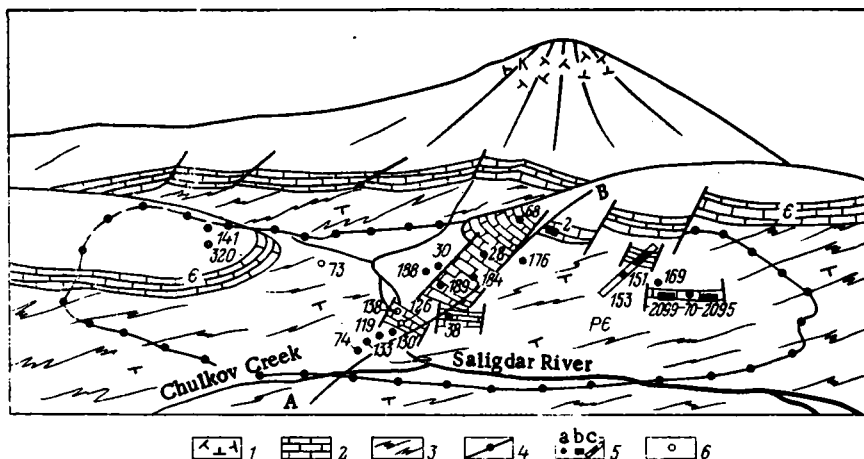


Fig. 1. Panoramic view (from the east) of the Seligdar ore deposit. 1) Syenite and monzonite of the Tommot massif (Bat'ko Peak) (K); 2) Yudom dolomite (€); 3) schist, gneiss, marble, and calciphyre (P€); 4) general outline of the Seligdar deposit; 5) sandstone localities: a) drill hole, b) prospect pit, c) trench; 6) other drill holes.

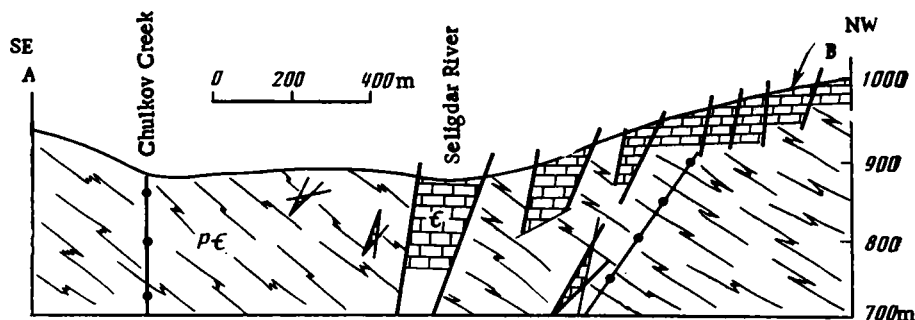


Fig. 2. Proposed cross section of block faulting. See Fig. 1 for explanation of symbols and section line AB.

of various thicknesses concordant with the apatite ores. It was indicated that marly clays locally occurred in the ores along with the sandstones. Since then, the presence of horizontal interbeds of sandstone, marl, and other apatite-bearing sedimentary rocks has been commonly considered a typical feature of the Seligdar deposit.

Systematic investigation of cores of all sandstones previously indicated to be apatitic and apatite-bearing showed that not all of them contain apatite, and that those containing clastic grains of apatite are from different geological positions. The locations of clastic rocks in drill holes or mine workings are shown in Fig. 1. They can be divided on the basis of geologic setting into the following four groups.

The first group consists of apatitic sandstones and grits that occur within the Yudom dolomite sequence. They are exposed in pit No. 2 in the lower part of the Yudom, where they are found to directly overlie an erosion surface on the ore body. The sandstones and grits form tabular lenses 0.5-3 cm thick in fine-grained dolomites. The sandstones are composed of clasts of monocrystalline quartz (30-40%), feldspar (15-30%), and apatite (30-50%), and also contains fragments of quartzite, microquartzite, apatite-bearing quartzose and feldspathic rocks, and individual grains of tourmaline, zircon, and biotite. Features of most interest are: a) well rounded and sorted quartz and feldspar grains with poorer rounding of apatite grains, which generally fall into the category of subrounded; b) large size of apatite grains relative to quartz (Fig. 3); sample 2 demonstrates this type [8]; c) predominance of potassium feldspar, including perthite and microcline, over plagioclase, indicating erosion of acidic crystalline rocks: granites or gneisses. The feldspar is generally pelit-

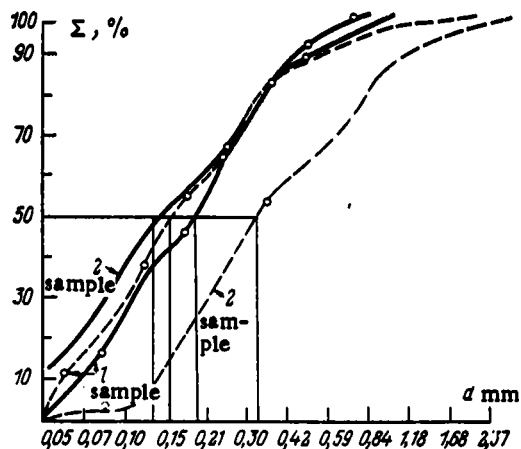


Fig. 3. Cumulative curves for quartz (solid lines) and apatite (dashed lines) showing grain diameter in this section with positive (sample 1) and negative (sample 2) size displacement. Median value for quartz (Q) and apatite (Ap), adjusted for the effect of the section cut is given by $M_{\text{true}} = M_{\text{apparent}} \times 1.32$; sample 1, $M_{\text{true}}(\text{Q}) = 0.26$, $M_{\text{true}}(\text{Ap}) = 0.20$; sample 2, $M_{\text{true}}(\text{Q}) = 0.17$, $M_{\text{true}}(\text{Ap}) = 0.42$.

ized, sometimes with regenerational borders. Basal or porous-basal type cement is dolomite of various degrees of crystallinity. Pore fillings are spotty to uniform, and amount to 30-40% of the rock. Zones of transition to sandy fine-grained dolomites were found in which the amount of apatite increased, rounding of all grains uniformly decreased, and corrosive action of the cement became greater. Dolomitic sandstones and sandy dolomites are associated with a gradual transition to dolomite devoid of clastic material.

At the base of the Yudom suite, generally at the base of sandy lenses, carbonate-free sandstones and grits are also found. They are composed of coarse clasts of granoblastic quartzite, monocrystalline quartz clasts, individual grains of weathered feldspar, and numerous fragments of apatite which make up as much as 40% of the rocks. The apatite clasts are as large as or larger than the quartz clasts. As in the case of polycrystalline quartz, individual fragments of apatite crystals reach 5-8 mm in size. The apatite grains are always less rounded than the quartz. The cement is pore-filling and continuous, pelitomorphic, ferruginous, and possibly apatite-bearing. Carbonate and noncarbonate sandstones are weakly altered, corresponding to the zone of moderate catagenesis.

The second group of clastic rocks combines occurrences both at the surface and at depth. This group mainly includes clastic rocks with apatite (sandstone, grit, conglomerate, breccia, etc.) exposed in trenches 153, 2095, and 2099 with the trench sections 10-30 m long. Sandstone and grit occurrences 10-30 m deep (holes 28, 151, etc.), which overlie and also underlie carbonate apatite ores, are also placed in this group. The tectonic nature of these sandstone blocks, which are small (0.7-1.2 m long in core) tectonic wedges inserted into carbonate-apatite ores, is clearly shown in cores (Fig. 4).

The conglomerates, with sandstone as cement, contain as much as 40% clasts of carbonate-apatite ore, quartzite, and a few other apparently metamorphic rocks, ranging in size from 3 to 40 cm. The sandstone cement, as well as sandy rocks without coarse clasts, are silica-quartz-apatite varieties that differ little from rocks of the first group. The sandstones are poorly sorted. The coarsest clasts are apatite, metaquartzite, microquartzite, and locally mica-quartz schist. The apatite grains, despite their large size, are generally more poorly rounded than the quartz and quartzite clasts, which indicates their provenance. It is interesting that among the gravels are found clasts of quartzitic sandstone which apparently contain crushed grains (?) of apatite of apatite cement. The ratio of components is highly varied, and a relationship to size was found: in coarse sediments more apatite was found than in others. There are grits that contain 60-70% coarse, locally angular clasts of apatite. The ratio of components in grits and sandstones is as follows: 30-60% apatite, 40-60% quartz, quartzite, and microquartzite, 5-15% feldspar, generally pelitized, 5-10% opaque altered clasts. There are also clastic grains of sphene, zircon, and opaque ore minerals.

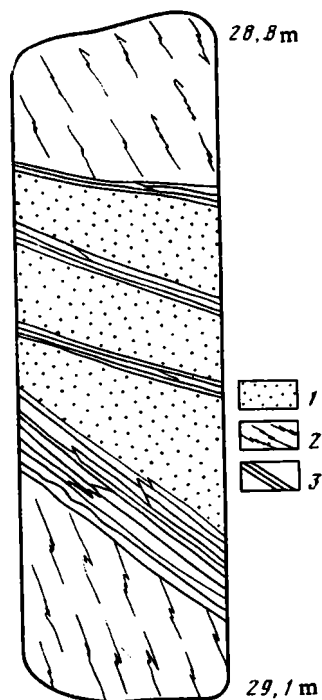


Fig. 4. Tectonic wedge in apatite-dolomite rock. 1) Sandstone; 2) apatite-dolomite rock; 3) mylonite (sketch of core).

The cement is either carbonate or composite, in stages. In the latter case the earliest stage is quartz cement, mostly regenerated, leading in many cases to conformal and blastic fusion of grains. It commonly corrodes apatite clasts, leading to irregular shapes or breakdown of coarse grains into fragments. Amorphous patchy cement, composed of pelitic ferruginous material, as well as dolomitic cement, in pore spaces and voids were emplaced later. These types of sandstones and grits are shown in Fig. 5.

An increase in the carbonate content leads to sandstones with dolomite and ferruginous dolomite cement. The transition to dolomitic sandstone is accompanied by a decrease in clast size (to coarse-grained sand, i.e., 0.5-2.0 mm), a decrease in amount of apatite grains, and a loss of secondary quartz cement. As before, apatite grains are larger and less rounded than other clasts and are commonly corroded and partially salted to dolomite.

Dolomite-cemented sandstones grade into sandy dolomite containing about 10% coarse, rounded grains of quartz and feldspar, including microcline. Rocks of the second group, as in the first, are weakly altered: they do not exceed the zone of profound catagenesis.

There is reason to believe that sandstones of the second group are part of the Yudom suite, involved in the ore body as a result of fault movement with formation of tectonic breccia. This is indicated by the following.

1. Abundant faulting in the region of the ore deposit, with large-scale displacement. Such faulting has been described in [1]. As an example, we point out that holes 126 and 136 were drilled on the bed of the Seligdar River 145 m below the level at which the base of the Yudom dolomite is usually found, but both holes encountered Yudom dolomites from the collar down to 110 m (hole 126) and 50 m (hole 138). Below that, down to the mine shaft (310 m in hole 126 and 174 m in hole 138), the core is composed of tectonic breccia and mylonite in blocks of Yudom dolomite, serpentized and chloritized gneisses, schists, and apatite-dolomite ore. The vertical displacement is estimated to be about 200 m, the fault plane is inclined, and the time of faulting is post-Yudom, apparently Mesozoic.

2. The lithologic similarity between rocks of this group and rocks at the base of the Yudom suite in composition of clastic material and cement, and the nature of the transition into low-sand dolomite of the Yudom type.

3. The degree of secondary alteration, which corresponds to the zone of catagenesis and is close to the alteration level of the Yudom rocks. At the same time, the relatively weak alteration of sandstones of this group contrasts sharply with the metasomatic alteration in the ore body and the high degree of metamorphism of surrounding rocks of the Iengr series. The sandy rocks differ from both in degree of alteration.

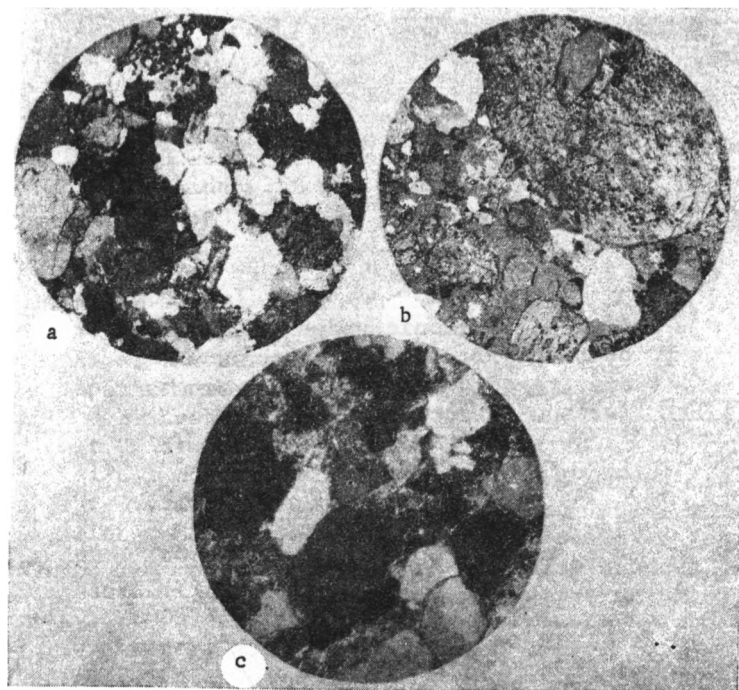


Fig. 5. Apatitic Sandstone of Seligdar River basin. a) Quartz-apatite sandstone, general appearance ($\times 15$); b) crystals of apatite in sandstone shown in Fig. 5a ($\times 45$); c) apatitic feldspar-quartz quartzite-sandstone.

The third group is composed of rocks found in the cores at various depths: 17 m (hole 130), 25 and 127 m (hole 133), and others, in intervals 20-30 cm in length. The sandstones in these occur within apatite-bearing carbonate rocks (ore) and have sharp, straight contacts, and are inclined at an angle of 30° from the axis of the core, parallel to the dip of the beds in the folded structure of the ore deposit. They are quartzose (85-90% quartz), fine- to medium-grained sandstones with a low apatite content (3-5%) and minor feldspar (3-10%). The sandstones are light gray, homogeneous, and dense. Traces of thin horizontal beds and cross-bedding are seen in the cores. Under the microscope, it is seen that quartz grains 0.2-0.5 mm in size, which are monocrystals or rarely polycrystalline fragments with a metamorphosed appearance, predominant. Apatite clasts are found as rounded grains similar to the quartz in size and shape. They are sometimes coated with a noncrystalline weathering rind. Granular calcite crystals, amounting to 5-8%, as well as knots of noncrystalline translucent material, are found in pore spaces and isolated areas.

Secondary quartz cement, conforming to the texture of sandstone, is characteristic of the rock. Compared to other sandstones, rocks of this group are highly altered and can be referred to the zone of epigenesis. The fourth group is a variety of rocks which are geologically obscure: contacts with adjacent rocks are generally penetrated by drilling, but the cores are very poorly preserved and yield no useful data. In composition they include sandstones, grits, sandy carbonates, and sandy dolomites with and without apatite. They are found at various depths from the surface: to 50 m (15 occurrences), to 100 m (another 7), to 150 m (another 8), to 180 m (2), to 210 m (1). Judging from the core, they occur within the ore at intervals (in core length) of 0.2-14.6 m, averaging 2.8 m, in which core length of sandstone and grit does not exceed 2 m in 50% of the cases, and only 14% exceed 10 m.

Analogues of dolomite, sandy dolomite, and sandstone of the Yudom suite are recognized in this group. Sandy rocks of other types also occur. Among these, feldspathic quartzose medium- to coarse-grained sandstones differ the most from rocks of the Yudom suite. They were encountered in core hole 70 at a depth of 38-43 and 56-66 m, and in core hole 73 at a depth of 36-37.5 m.

The rocks are gray with distinct ash-gray and chalky alteration traces, massive structure, and uniform texture. They are characterized by a predominance of grains of quartz (50-65%) 0.4-0.5 mm in size and feldspar (25-35%). Apatite grains are isolated, no more than 3-5%. The size change coefficient for grains of apatite and quartz is positive (see Fig. 3, sample 1). Quartz is monocrystalline; polycrystalline grains and microquartzite are rare. Feldspar is alkaline, always broken down: generally sericitized, sometimes pelitized. Many

clasts have been completely replaced by fine-grained sericite flakes and crushed by the harder quartz grains, which creates the appearance of a sericite cement (see Fig. 5c). About 5% of the rock is composed of structureless, weathered, limonitized grains. These are crystals and aggregates of secondary epidote, clastic zircon, and grains of apatite, which are rounded or idiomorphic prismatic with slightly worn edges. The texture is conformal; microstylolitic grain contacts are found, but refenerated faces are rare because of reworking of the original grain surface. These sandstones differ from other types by their very high degree of alteration, which, from textural characteristics, corresponds to the zone of profound epigenesis.

* * *

In both manner of occurrence and petrographic character, apatitic clastic rocks are morphologically, and apparently genetically, diverse. They are all sedimentary, and also the apatite contained in them is in large part clastic, but its formation took place at various times and in various conditions. Rocks of the first, second, and part of the fourth groups (sandstones, pebbly sandstones, grits, and conglomerates) belong to the Yudom suite and occur either within the stratigraphic sequence of the upper structural level or as tectonic fragments carried down along faults. By nature, these rocks are products of the mixing of various sedimentary materials, on the one hand local, associated with the breakup of the ore banks made up of Lower Cambrian rocks of the Seligdar deposit, and on the other hand, brought in from afar, essentially quartzose, with well rounded and sorted grains. Upon a certain amount of reworking and transportation, at first a quartz-apatite sandstone with displacement of the large median grain size toward the heavy mineral, apatite, is formed. On further transport, apparently minor, since different types of apatite-bearing rocks occur next to one another, the normal ratio of heavy and light minerals for terrigenous rocks was established.

Formation of the basal beds of the Yudom suite took place on a highly dissected surface, as shown by lack of rounding of large blocks of carbonate-apatite ore included in the sandstones, and also by the presence of large crystals and fragments of apatite. The burial of the Precambrian surface of relief can apparently be partially explained by the different elevations of apatitic sandstones at the base of the Yudom. These differences could have been increased by later block faulting.

The considerable chemical stability of apatite should be emphasized; despite the variety of rocks forming the ore banks in the Seligdar headwater deposits, only fragments of apatite and carbonate apatite are found in the erosion products. The other rocks in the area, serpentinitic and chloritic metasomatites in schists and gneisses, apatite-carbonate rocks and the minerals forming them (calcite, dolomite, chlorite, serpentine, martite, talc, gypsum, etc.) were apparently broken down by weathering processes during pre-Yudom and Yudom time, and the products of abrasion of these minerals formed the fine fraction of pelitic sediments.

Sandy rocks that differ petrographically from the Yudom, found within the metasomatite sequence (third group) or in an obscure geological setting (some fourth group rocks), may be older than the Yudom suite, possibly Precambrian. According to Éntin et al. [9], there was a stage in the evolution of the Seligdar region between ore deposits, occupying the interval 1.8-1.4 billion years ago when the Seligdar graben was formed, in which a terrigenous-carbonate-volcanic sequence with reworked apatite in sandstone, grit, and breccia was deposited. It is also possible that the sandstones we described in the third and fourth groups are still older and are part of the principal ore-bearing sequence of early Precambrian age. Both of these views are debatable. The problem of the occurrence of apatite sandstones older than Yudom, as in the older Proterozoic rocks as well, can apparently be resolved outside the area of the Seligdar deposits, where tectonism and metasomatism were less intensive.

In interpreting the origin of sandy blocks found within the ore body, it is necessary to consider that almost everywhere they occur in elongate belts (see Figs. 1 and 2) along a zone of intensive fault displacement, as determined by the base of the Yudom suite (holes 28, 30, 38, 68, 74, 119, 176, 188, 189, and prospect pit 2). Only three holes (73, 141, 320) with cores containing sandstone beds occurred far away from the fault zones. This conspicuous restriction of sandstone occurrences to the fault zone sheds light both on the nature of the sandstones included within the ore body and on the significance of the faults forming the block structure of the ore field. The apatitic grits and sandstones are so unique in composition and texture, that they are one of the most interesting geologic discoveries in South Yakutia in recent years. Further work on these rocks is needed to obtain more details,

on the basis of new data, on their lithologic features, development, and stratigraphic position in the Aldan platform deposits.

LITERATURE CITED

1. A. G. Bulakh and A. A. Zolotarev, "Geologic nature of the Seligdar apatite-carbonate field (Aldan Shield)," *Sov. Geol.*, No. 6, 96-101 (1983).
2. A. G. Bulakh, A. A. Zolotarev, I. P. Bubrova, et al., "Basic features of the mineralogy and origin of the Seligdar apatite deposit (Aldan Crystalline Shield)," *Zap. Vsesoyuz. Mineralog. o-va*, 113, No. 4, 398-410 (1984).
3. E. K. Gerasimov, "Terrigenous deposits of the Seligdar apatite deposit," *Tr. SNIIGGIMS, Novosibirsk*, 218 (1976).
4. E. K. Gerasimov, M. V. Sukhoverkhova, R. G. Matukhin, et al., "Structure of the Seligdar apatite ore field; Aldan Shield," *Dokl. Akad. Nauk SSSR*, 250, No. 3, 675-679 (1981).
5. I. P. Kusharev and A. D. Cherkasov, "Structure and origin of the Seligdar apatite deposit," in: *Methods of Prediction and Evaluation of Exogenic Rare Metal Deposits* [in Russian], Moscow, VIEMS (1979), pp. 63-85.
6. V. D. Parfenov and N. I. Yudin, *Ancient Metamorphosed Apatites of Central Asia* [in Russian], Moscow, Nauka (1982).
7. F. L. Smirnov, *Geology of the Apatite Deposits of Siberia* [in Russian], Novosibirsk, Nauka (1980).
8. V. N. Shvanov, "Distribution of minerals in size fractions of sands deposited by wind and water," *Vestn. Leningrad. Gos. Univ.*, No. 6, 155-159 (1964).
9. A. P. Éntin, É. V. Sobatovich, Yu. A. Ol'khovik, et al., "Conditions of formation of the Seligdar apatite deposits (Central Asia)," *Sov. Geol.*, No. 8, 17-27 (1984).

PRIMARY STRUCTURES OF SULFUR ORES AND THEIR CLASSIFICATION

S. K. Kropacheva, L. S. Sonkin, and V. E. Ponomarev

UDC 553.66:553.06

The findings are presented of a study of inherited structural and textural features of sulfate rocks in metasomatic sulfur ores. On the basis of these features, a classification of primary structures of ores is suggested and a brief description of the ore types is given.

Commercial exogeneous sulfur deposits are confined to halogenic formations and are well known [8-10] to occur amid calcium sulfate sediments; gypsum and anhydrite contained in them are the source of authigenic sulfur and secondary metastomatic calcite.

Infiltrational sulfur metasomatism, acknowledged currently by most investigators [4, 6, 7, 9, 10, 13, 14, 17, etc.] is confirmed both by general geological theories and the results of lithological and petrographic studies. Direct evidence for the substitution is given by the numerous finds of pseudomorphoses of joint calcite and sulfur aggregates or of either mineral found in the ores which developed after calcium sulfate crystals [6, etc.]. Metasomatic microstructures identical in appearance to the initial sulfate rocks are common in sulfur ore [13, 14]. Studies at some of the deposits have determined that terrigenous impurities in the ores and in the corresponding varieties of predecessor sulfate rocks are present in comparable quantities [3, 4].

Obviously, the textural and structural features of metasomatic sulfur are closely related to those of the sulfate rocks they replace. Studies of sulfur ores, however, encounter difficulties with the exact determination of the structures of sulfate predecessor rocks. Some investigators established a positive correlation, but other studies failed to yield classifications of primary structures in terms of inherited features [2, 6, 14]. This was

Ministry of Geology of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 78-90, May-June, 1986. Original article submitted March 15, 1985.

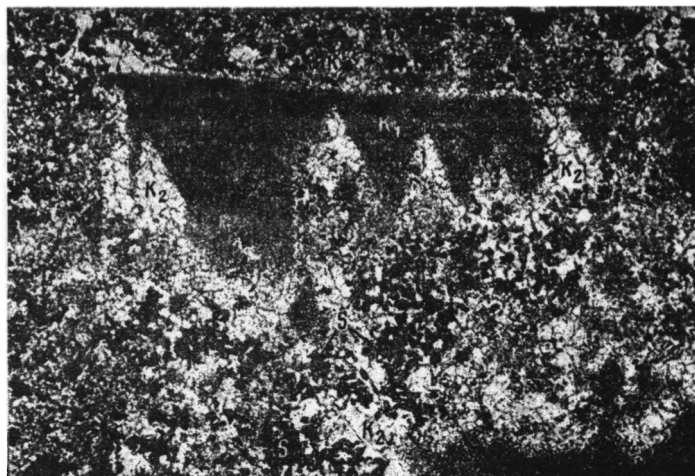
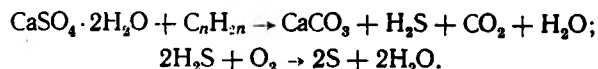


Fig. 1. Metasomatic substitution of an aggregate of finely dispersed cryptocrystalline sulfur (S) and calcite (K₂) for large gypsum crystals. The photomicrograph shows relicts of sedimentary limestone (K₁), which underline the contours of the tops of replaced gypsum crystals. The predecessor was a carbonate-sulfate rock with macrocrystalline gypsum structure. Zagaipol deposit (Cisearpathian region), core, single nicol, ×40.

due to a lack of studies of predecessor rock structures. Later [13], a classification of structures of sulfate and carbonate-sulfate rocks according to the morphogenetic features was constructed. The primary (syngenetic) and secondary structures were identified; the secondary structures replaced the primary structures during postsedimentary stage of rock evolution.

Based on this classification of productive rocks and the data from the studies of the various structures of sulfur ores in two regions of commercial sulfur production (Cisearpathian area of the Ukraine and Gaurdak-Kugitang region in Turkmenia), the present authors tried to determine the principal primary ore textures on the basis of characteristics inherited from primary sulfate rocks. In order to clarify the authors' notion of the "primary" structure, certain aspects of the metasomatic process of sulfur formation should first be outlined.

The chemistry of infiltrational metasomatism after calcium sulfate is complicated and not perfectly clear. Many investigators [3, 15, etc.] believe that it occurs as a two-phase microbiological process. The first phase is sulfate ion reduction to hydrogen sulfide by sulfate-reducing bacteria in the presence of carbonic matter; the second phase is hydrogen sulfide oxidation by oxygen-containing water to authigenic sulfur. Carbon dioxide formed during the sulfate reduction has hydrocarbons are oxidized reacts with the calcium released from sulfate minerals and precipitates in a carbonate form. Both phases are assumed to be separated either in time or in space, because reactions in reducing and oxidizing media are unlikely to concur within the same closed volume. Generally, the two-phase sulfur formation process can be described as follows:



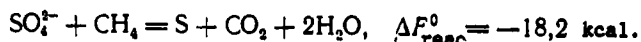
Petrographic studies do not always confirm the two-phase metasomatic sulfur formation; for such a process only calcite pseudomorphoses are more likely to develop after gypsum crystals (the first phase), and the sulfur inclusions should be found in the interstices between them (second phase). Along with these forms of metasomatism, aggregate joint calcite and sulfur pseudomorphoses, after sulfates, are quite widespread in the ores (Fig. 1). The fine intergrowth of metasomatic minerals seems to suggest a single-phase process. The probability of this kind of metasomatism was noted earlier by Sokolov [10, 11]. Although experimentally this theory has not been confirmed as yet, the presence of numerous metasomatic sulfur deposits at depths inaccessible to oxygen-saturated surface waters, not to mention liquid sulfur

TABLE 1. Types of Widespread Primary Structures of Sulfur Ores Inherited from Parent Sulfate Rocks (with special reference to Ciscarpathian sulfur basin and Gaurdak-Kugitang region)

Sulfate and carbonate-sulfate rocks common in sulfur deposits	Sulfur ore structures		Form of sulfur segregations	Occurrence in sulfur-bearing regions
	Morphologic group	Morphogenetic variety		
Horizontally stratified purely sulfatic rocks and their recrystallization products: homogeneous, massive small-grained anhydrite and geothite	No sulfur ore formed			Ciscarpathian region, Gaurdak-Kugitang region
Clay-sulfate rhythms	"			"
Interstratified sulfate and carbonate rocks	Elongate	Inherited fine-stratified	Striated, finely disseminated Lenticular, dispersely scattered	"
		Inherited, coarse-stratified		"
Porphyritic carbonate-sulfate rocks and rocks formed after them by sedimentary alteration, with reticulate, meshlike, variegated, enterolitic, and other structures	Porphyroid	Inherited disseminated Inherited nodular Inherited nestlike, maculose Inherited reticulate	Disseminated, nestlike, maculose, veinous, dispersed Dispersely disseminated with microinsets	"
	Massive (solid)	Homogeneous with small sulfur insets		"
Rocks with macrocrystalline gypsum textures, with subvertically oriented crystals 1) Coarsely stratified monomineral primary gypsum and massive small-grained anhydrite formed after it and secondary gypsum	No sulfur ore formed			Ciscarpathian region
2) Massive carbonate-sulfate rocks and maculose calcareous anhydrite and secondary gypsum formed after them	Elongate	Elongate-maculose, elongate-nestlike	Subvertically positioned elongate nests, spots, often distinct pseudomorphoses after large gypsum crystals	"
Stromatolitelike rocks originating from sulfatization of stromatolitic bioherms 1) Pure sulfatic	No sulfur ore formed			"

2) Carbonate-sulfatic	Elongate	Inherited	Striated, maculose, dispersed-scattered	"
2) Carbonate-sulfatic	Porphyroid Massive (solid)	Stromatolitic Homogeneous with small sulfur segregations	Disseminated, nestlike, dispersed-scattered Dispersed-scattered, micro- disseminated	"
Clastic sulfatic and carbonate-sulfatic rocks	Clastic	Inherited breccia and breccialike Inherited boudin- age texture	Disseminated, nestlike, maculose, veinous	Ciscarpathian region Gaurdak-Kugitang region Gaurdak-Kugitang region

(depths of 3-6 km) [16] seems to confirm Sokolov's hypothesis of the possibility of single-phase abiogenic sulfate reduction to elemental sulfur. In this process, reduction does not achieve the stage of formation of hydrogen sulfide. Thermodynamically, such a route is not impossible. For example, the free energy of sulfate reduction to sulfur, for example by methane, even in standard conditions, has a negative value:



In authigenic sulfur deposits, metasomatic alteration is mostly experienced not by pure sulfate rocks but by carbonate-sulfate rocks due to their better permeability to water-hydrocarbon fluids. The permeability of rocks of the mixed composition is due to the anisotropy of their physical and mechanical properties because of the presence of inclusions of sedimentary limestone [13]. Solid pure sulfate rocks or clay-sulfate rocks, on the contrary, are water-resistant and susceptible to metasomatic alteration only when they are fractured by intense tectonics, which is not the case in many of the deposits.

When carbonate-sulfate rock is replaced by calcite, authigenic sulfur, or minerals paragenetic with it, the main alteration in the composition of the parent rock occurs initially in the sulfate component, which is represented either by gypsum or anhydrite, or by both minerals in combination. The principal process at this mineralization stage is gypsum replacement by calcite of metasomatic generation, sulfur, celestite, and less often barite;* anhydrite merely experienced hydration during the premineralization stage. It has been established earlier [6] and confirmed by our study that sedimentary calcite portions pass into the ore with intact composition and hardly any textural alteration. The neomorphs of metasomatic calcite can consist of grains of different size, including fine-grained varieties which are similar to sedimentary generations of carbonate. In the latter case, both macroscopically and in polished sections, it is difficult to draw a distinction between relict segments of chemogenic limestone inherited from sulfate rock and the metasomatic calcite [14]. Petrographically, this differentiation is possible only when pseudomorphoses after sulfate crystals have been preserved or on the basis of isotopic analysis of carbon in different carbonate generations. Because pseudomorphoses are often lost subsequently during recrystallization of sulfur ores and isotopic analysis of recrystallized calcite yields average values, identifying the primary metasomatic textures of ores from the most widespread polygenic calcite is virtually impossible.

The degree of crystallization and texture of authigenic sulfur is also insufficiently informative for classifying structures on a genetic basis common for the deposits studied. In the Carpathian region, for example, it has been determined [5, 12, 15, etc.] that the earliest generation is cryptocrystalline sulfur, while in the Gaurdak-Kugitang area such sulfur textures are observed only in later sulfur generations, in particular in sediments redeposited in karst cavities. Metasomatic sulfur always has a phanerocrystalline texture [15] in that region.

It is thus impossible to construct a general classification of primary textural-structural features of ores for the sulfur deposits studied on the basis of the textures of polygenic calcite and the size and crystallization of sulfur individuals. A more informative aspect of the primary build of the ore is its structural characteristics inherited from sulfate rocks. Sulfur metasomatism produces sulfur ores replacing sulfate-bearing rocks; the structures of these ores originally always repeat those of the parent rock. The sulfate component of the parent rock is replaced by neomorph aggregates which bear the same relationships to the relicts of sedimentary limestones as the original sulfate and carbonate in the rock of the mixed composition prior to substitution. These structures should be regarded as "primary," regardless of the textural features of sulfur or its paragenetic calcite. Whether the sulfate-bearing rock which experienced metasomatism had syngenetic structures or secondary structures caused by postsedimentary alteration is immaterial.

The structural features of sulfur ores inherited from sulfate rocks have been used as the basis for the classification of structures compiled by the authors.

*Strontium and barium are contained either as isomorphous admixtures in anhydrite (gypsum) or as minerals syngenetic to them. Metasomatism releases the isomorphous admixtures, which then precipitate as low-soluble sulfate (barite or celestite). Segregations of these minerals of premineralization stage present in the parent rock remain in the ore with virtually unaltered composition and shape.

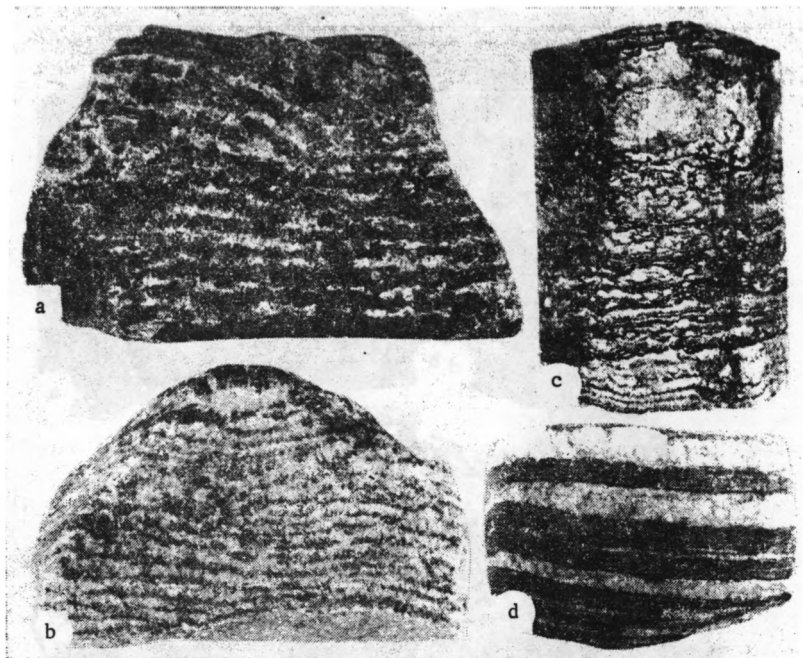


Fig. 2. Specimens of sulfur ore with inherited finely stratified structure. a) Podorozhnenskoe deposit, Ciscarpathian region; b) rhythmic-striated ore from Gaurdak deposit, reduced 2 $\times$ (light: sulfur; dark: calcite); c) original sulfate-bearing sediments after which ores of similar structures developed (fibrous-stratified calcareous anhydrite), Kyzyl-Tumshuk (Turkmenia); d) coarse anhydrite/limestone interstratification from Gaurdak deposit (d), core, reduced 1.5 $\times$ (light: anydrite, dark: limestone).

Table 1 gives a correlation of the structures of sulfate predecessor rocks and the structures of metasomatic sulfur ores formed after them. The morphogenetic varieties of ore structures are distinguished by the features of their inheritance from metasomatically altered rocks. The varieties are brought together into morphological groups, as is usual in studies of ores of various minerals. The nomenclature is based on the classification scheme of Isaenko [1].

Table 1 takes into account morphological features of authigenic sulfur, which are usually included in geologic-industrial classifications of sulfur ore [5, 12, 14]. The data indicate that the form of sulfur inclusions in ores with different structures inherited from predecessor rocks in many cases is the same. This demonstrates the poor informativity of the morphology of sulfur isolates as a feature for classifying the metasomatic ore structures on a genetic basis.

The most common inherited primary structures of sulfur ores are described below.

Ores of an elongate structure are widespread in all sulfur deposits of the Ciscarpathian region and Turkmenia. Most common are inherited stratified ore structures arising during metasomatism after fine (1-2 mm) wavy interstratification of carbonate and sulfate sediments typical for tidal plains (paleosebkha facies). Ore develops also after alternating, even, coarser (from 1 cm and more) layers of similar rocks. These structures are stable and can be detected even after the superposition of all later processes. Rhythmic fine-striated ores, for examples, which are common in all sulfur deposits, originate from altered inherited structures of fine-stratified carbonate-sulfate rocks. The inherited nature of the stratification in the ore of Razdol deposit has been investigated in detail in an earlier publication [6].

When ore was formed after interstratified sulfate and carbonate rocks, only sulfate layers were first replaced by sulfur and secondary calcite. The sedimentary calcite layers

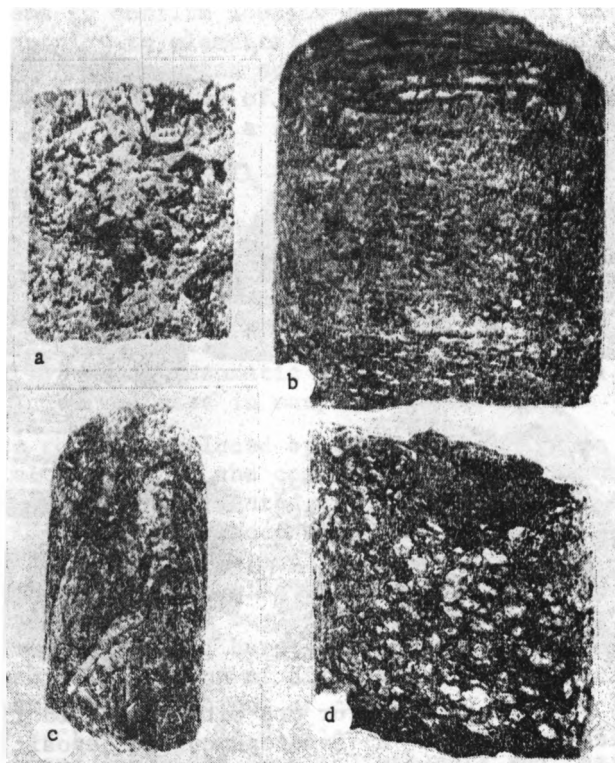


Fig. 3. Sulfur ore of elongate-nestlike (a) and inherited densely disseminated (b) structure, Grim-novo deposit, core, actual size (light: sulfur, dark: fine-grained calcite); c) macrocrystalline gypsum for sulfate bed, Nemirov deposit, core, reduced 1.2 $\times$; d) calcareous anhydrite of a small-nodular structure (Shevchenko deposit), core, reduced 1.2 $\times$ (light: anhydrite, dark: limestone).

experienced slight recrystallization. During the postmineralization stages, the degree of mineralization increased because of redistribution of sulfur, and dark sedimentary (usually pelitomorphous) calcite was altered into light coarser-grained varieties. As a result, striated ores arose whose relict stratification is seen only in the change of color of inequigranular-calcite and uneven distribution of sulfur mineralization. Figure 2 illustrates the characteristic ore structures of this variety and the initial stratified carbonate-sulfate rocks.

Another type of structure of this morphological group is elongate-nest or elongate-variegated. It is formed during metasomatic alteration of sulfate rocks with structures of macrocrystalline gypsum, typical only for Ciscarpathian profiles. The ore with elongate-nest structure has been found exclusively in the Ciscarpathian regions. The parent rocks usually include idiomorphous primary-sedimentary gypsum crystals positioned perpendicular to the bedding plane. Sedimentary limestone areas of a peculiar shape are squeezed between these. During dehydration, these rocks are transformed into calcareous elongate-variegated anhydrides with spots due to elongate anhydrite pseudomorphoses after gypsum. During the formation of the ore, the primary gypsum crystals (or anhydrite pseudomorphoses after gypsum crystals deformed by hydration that preceded the ore formation) are transformed into elongate nests or spots consisting of sulfur or calcite aggregate and retaining a subvertical orientation relative to the bedding surface. Contours of crystals of replaced gypsum sometimes are preserved well during the metasomatism. Segments of sedimentary limestone pass into the ore almost unaltered. Figures 3a and c illustrate the ores of this structure and the parent macrocrystalline gypsum.

Ores of elongate-nest variety have for a long time attracted the attention of investigators in the Precarpathian basin. Distinct large sulfur and calcite pseudomorphoses after

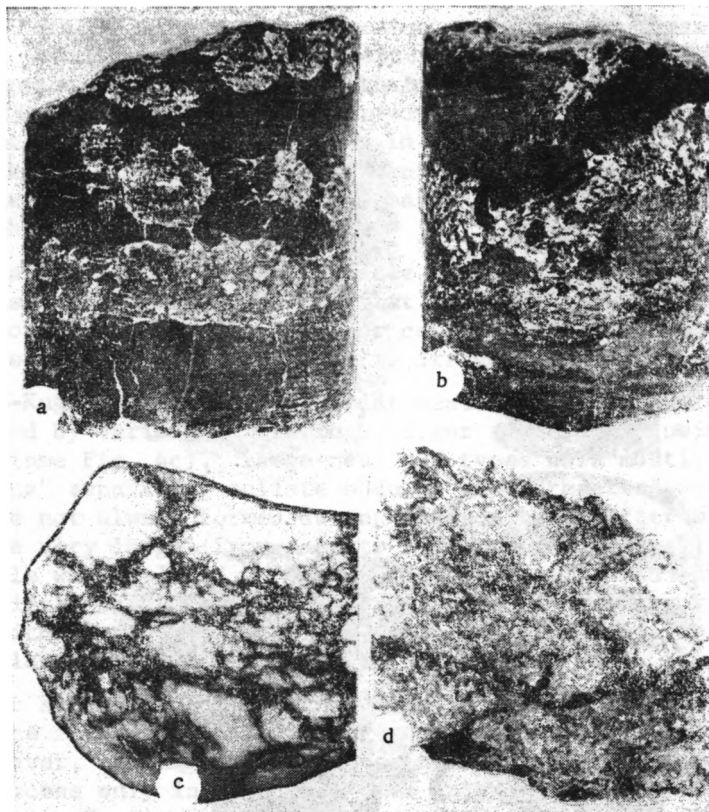


Fig. 4. Sulfur ores of an inherited porphyrytic structure: a) sulfur ore with primary veinous-nodular structure, Grimanov deposit, Ciscarpathian region, core, actual size (parent rock: carbonate sulfate, of coarse-nodular structure with epigenetic gypsum veinlets; b) sulfur ore with primary nestlike structure (Yazov deposit, Ciscarpathian region), core, actual size (stromatolitic features preserved in the relic limestone; most sulfate inclusions in the original carbonate-sulfate rock were deformed nodules); c) specimen of calcareous anhydrite of coarse-nodular structure, from quarry in Gaurdak deposit, reduced 2× (light: anhydrite; dark: limestone); d) sulfur ore of inherited reticulate structure with large-nest sulfur segregations (Kyzyl-Tumshul, Turkmenia), core, actual size (light: sulfur; dark: fine-grained calcite).

so-called saber-shaped gypsum crystals have been sometimes observed in them. These served as one of the first proofs of the metasomatic origin of sulfur deposits [2].

Similar conclusions for the Polish territory of the Ciscarpathian region were drawn earlier by Pawlowska [17]. The postmineralization stages blurred the characteristics of inheritance from macrocrystalline gypsum and they were partly lost. But for facies stability of the sets of initial deposits, identifying the ore masses formed after such sulfates is possible when relicts of the primary structures are present in the ore.

In addition to the above varieties, the group of elongate structures includes plane-elongate structures of sulfur ores inherited from the predecessor carbonate-sulfate rocks of stromatolitelike structures. They occur only in the Ciscarpathian sulfur basin. The initial rocks were formed during early diagenetic sulfatization of stromatolitic bioherms, which is observed frequently on tidal plains [13]. These rocks are often found in associations with macrocrystalline gypsum. Both are formed in similar facies settings.

Ores with inherited stromatolitic structures often are similar to those created by metasomatic alteration of interstratified carbonate and sulfate rocks. Both have sulfur segregation strips stretching in the horizontal or subhorizontal plane. The ores developed after stromatolitic rocks, however, display an inconsistent large-wavy striation resembling that

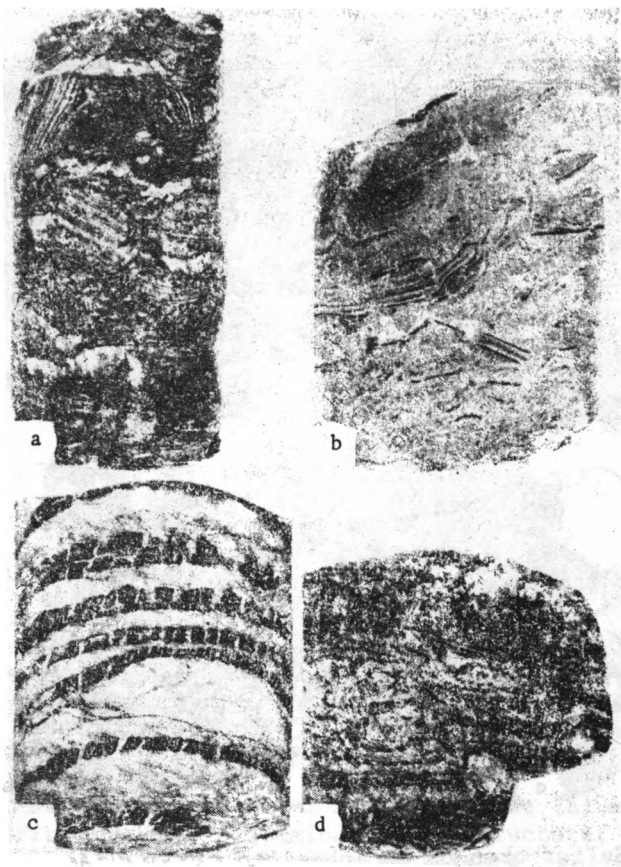


Fig. 5. Sulfate-bearing rocks with clastic structures and sulfur ores with similar inherited structures: a) tectonic breccia after fine-stratified clay anhydrite (Lisetsk sulfur show, Ciscarpathian region), core, reduced 1.5 $\times$; b) sulfur ore of inherited breccia structure (Grimnov, Ciscarpathian region, core actual size) (light: sulfur; dark: fine-grained calcite); c) interstratification of boudinaged limestone and anhydrite; dark: limestone); d) sulfur ore with inherited boudinage texture, same site, actual size (light: sulfur; dark: fine-grained calcite).

of stromatolites. The relicts of sedimentary limestone clearly reveal the stromatolitic nature of these units. Irregular spottiness is also typical of these ores. The weak sulfatization of stromatolites obviously leads to ores that developed after them with scarce insets of nests of sulfur replacing sulfate inclusions. A high degree of sulfatization of bioherms results in the formation of richer solid ores after stromatolitelike rocks. Mineralization often is represented by dispersed sulfur. The features of inheritance of stromatolitic structures in ores are quite frequent in the Ciscarpathian region. An example is given in Fig. 4b; here metasomatosis developed after sulfate nodules, which grew during the diagnosis of stromatolitic bioherms.

Ores with Porphyroid Structures. This morphological group includes the varieties created by alteration of carbonate-sulfate rocks consisting of individual sulfate minerals or isolated aggregates of the minerals scattered in sedimentary limestone. These structures are observed in peculiar mixed-composition rocks which were formed in a paleosebkha setting and are widespread in all sulfur deposits [13].

In the Ciscarpathian region, the ores with inherited porphyroid structures consist of disseminated, nodular, variegated, and nest types. Disseminated ores were formed after carbonate-sulfate and sulfate-carbonate rocks with small (up to 5 mm) sulfate inclusions. Depending on limestone saturation with these inclusions, rare- or dense-disseminated

ores were formed, because originally metasomatic alteration was experienced only by sulfate inclusions, while sedimentary limestone changed slightly. The ore structure at these early stages conforms fully to that of the parent rock (see Fig. 3b). During the postmineralization period, the sedimentary limestone was recrystallized, and superimposed sulfur mineralization could appear in it. In most cases, the inherited structure of sulfate rock could be recognized. When the sulfate rock had previously experienced some epigenetic alteration, including the formation of gypsum veinlets, the ore had a veinlet-disseminated inherited structure.

Ore with nodular structure developed after mixed carbonate-sulfate rocks with somewhat larger distinctly isolated nearly round or flat sulfate inclusions (see Fig. 4a). The sulfate inclusions deformed during diagenesis or catagenesis were converted by metasomatic processes into spots and nests of sulfur of an irregular shape (see Fig. 4b).

In the Gaurdak-Kugitang area, the parent mixed rocks of a porphyroid structure are typically represented by varieties with much larger sulfate inclusions measuring up to a few centimeters across (see Fig. 4c). Large-nest ore types were mostly formed after them, while carbonate "partitions" separating sulfate nodules were preserved as relicts (see Fig. 4d). Large-nest ores were not always formed during metasomatism after similar rocks. When the sulfate nodules were very large (from 5 cm to tens of centimeters), the sulfur within the contour of the nodule was isolated as small nests or insets amid the metasomatic calcite mass. Sometimes sulfur segregations were dispersed amid calcite or formed peculiar dendritoid concretions with them. Segments with small sulfur segregations could be contained in ore blocks with large-nest structure.

The metasomatic alteration of low-carbonate initial rock with so-called reticular structure often led to the formation of a rich ore with dispersed sulfur. The poor permeability of these units, however, was not conducive to intense metasomatism. They were involved in sulfur-formation process only in the zones with intense tectonic fracturing [4] and mainly in the direct vicinity of permeable carbonate-sulfate rocks more favorable for mineralization.

In the Gaurdak deposit, ores with secondary disseminated structures are widespread, which developed after the main stage of metasomatic mineralization. Yushkin [15] observed on the planes of the cracks crossing the sulfur ores with various primary structures a hydrogenic/superimposed sulfur mineralization in the form of small insets or round nests. In this region, when identifying the primary structures in porphyroid rocks, one should therefore be guided by the presence of sedimentary limestone relicts forming a distinct network in the rock rather than by the form of sulfur inclusions.

Ores of a Clastic Structure. The clastic structure in the ore can be inherited from clastic sulfate rocks of various origins (redeposited during sedimentary stage, tectonic breccias, dissolution breccias, etc.). As in other parent rocks, metasomatism occurs here in the sulfate components whether these are fragments or groundmass. In addition, sulfur mineralization (usually poor) is found sometimes in clastic nonsulfate rocks; it is not directly associated with metasomatic processes but is of a superimposed nature. Such rocks in the profiles of sulfur deposits studied are less frequent than metasomatic ores after sulfate breccias, although the two look similar at first glance.

Figures 5a and b shows breccias and ores with clastic structures. Breccias can be formed both after pure sulfate rocks and after mixed carbonate-sulfate rocks. Because of a high permeability, metasomatism develops intensely in both cases, and rich ore is formed.

Ore with inherited boudinage textures are frequent in the Gaurdak deposit. These structures arise in parent rock under certain tectonic movements on sediments consisting of interstratified plastic sulfate and more rigid carbonate rocks. Figures 5c and d show boudinaged fine carbonate interlayers alternating with thicker sulfate layers and sulfur ore created by metasomatic alteration of these sediments.

In the profiles of all the sulfur deposits studied are rich homogeneous ores of a massive solid structure, where features of inheritance from sulfate rocks are usually hardly noticeable or absent, making it difficult to place them in the classification of primary structures. This structural variety is characterized by uniform distribution of microscopic sulfur inclusions or sulfur insets measuring 1-2 mm across in the enclosing carbonate rocks, which have a microgranular texture. So far, none of the inherited primary structural varieties of ore described above has been known to be transformed into ore with a massive structure and small sulfur segregations. According to the data of a number of investigators [6, 14] and the authors' own observations, these massive ore structures must be primary.

In the Ciscarpathian basin, massive ores are represented by small-grained calcite with aggregates of fine-dispersed cryptocrystalline sulfur (primary generation) which occurs either as separated microscopic insets or as fine, peculiar concretions with calcite. Ores of this type have been studied in detail at Rozdol deposit. According to Merlich and Datsenko [5], they are concentrated mainly at the top of the deposit. Visual observations can leave an impression that the ores with such structure are developed after monomineral massive fine-grained sulfate rocks. This is contradicted by the quantity of clay admixture present in them. The same authors [5] report clay contents up to 5%, while in the sulfate rocks studied by them it is not higher than 2%. Such low contents are typical for massive monomineral sulfatic rocks, which is suggested by numerous determinations of the contents of terrigenous impurities in productive rocks of various morphogenetic types [3]. A comparison of these data with the amount of impurities in massive ores suggests that they were formed after mixed carbonate-sulfate rocks rather than after pure sulfate varieties. Some of the massive ores of this type contain shadow relicts of cleaved (stromatolitic) textures, indicating the development of metasomatism after stromatolites sulfatized during the diagenesis.

A detailed investigation of polished sections determines which of the rocks experienced metasomatism during the formation of the Ciscarpathian ores of the massive structure with dispersed sulfur. Judging by the few relict microstructures that have been preserved, these were carbonate-sulfate and sulfate-carbonate rocks of microdisseminated and microporphyroid varieties (closely situated microscopic inclusions of sulfate minerals distributed uniformly in pelitomorphic sedimentary limestone). This does not rule out the presence of sulfates in stromatolitelike formations.

Ore of a similar massive structure is also common in the Gaurdak deposit. Here it is usually described as uniform, with dispersed-scattered sulfur. As has been mentioned earlier, such ores often alternate with ores of other structural types. The contacts between these varieties are distinct. In contrast to Ciscarpathian ore, the sulfur is planarocrystalline. Visually and in polished sections, no features of inheritance from particular varieties of productive rocks have been observed. The issue can be clarified indirectly by studies of near-contact zones between sulfur deposits and adjacent sulfate rocks. Such observations confirm that the segments of ore with uniformly distributed dispersed sulfur were previously very large, purely sulfatic nodules in mixed carbonate-sulfate rocks of a large-nodular structure, which are currently found along the perimeter of ore bodies. Collective recrystallization, apparently at early postmineralization stages, formed even more uniform segments of solid (monomineral) sulfur from the massive ore.

* * *

The study has identified the primary structures of sulfur ores based on the theory of infiltrational metasomatism. Structural varieties in little-altered ore are determined easily. The procedure is more difficult in ore with a secondary structure. The presence of relicts of primary structure, which with rare exceptions are to some extent preserved in the profile, however, allows establishing for relatively large ore masses, stretching for tens of meters, the morphogenetic type of the original sulfate rock.

In addition to the theoretical interest, the classification of primary structures of metasomatic sulfur ore is important practically. The classifications of sulfur ore structures developed earlier, based only on morphology [4, 12, 14], for mapping the ores with various structures and various engineering properties (in particular, for extraction by underground sulfur melting [USM]) can no longer be considered satisfactory. With them, it becomes necessary to scrupulously document the core from each exploration bore hole, which prevents a uniform identification of large ore masses with similar textural-structural features, given the existence of a large number of transient structural varieties. Since morphogenetic types of the original productive rocks (microfacies) are consistent over large areas [13], the characteristics suggested by the authors can be used for geometric mapping of ores with similar primary textures, important for evaluating their USM technologies. A capacity for determining the primary ore structures consistently and easily also predetermines the possibility of a more detailed study and mapping of superimposed processes. This means an improvement of the methods establishing the correlations of the engineering properties of ore and its nature and other independent factors (tectonics, karst, hydrogeological settings, etc.). Generalizations of these data will help develop more efficient methods for predicting the engineering properties of ore during the reconnaissance stage.

LITERATURE CITED

1. M. P. Isaenko, Identifier of Ore Structures and Textures [in Russian], Nedra, Moscow (1975).
2. V. I. Koltun, "Genesis of sulfur deposits of Ciscarpathian region based on lithologic data," in: Geology and Geochemistry of Sulfur Deposits of the Ciscarpathian Region [in Russian], Naukova Dumka, Kiev (1966), pp. 12-20.
3. S. K. Kronacheva and V. E. Ponomarev, "The nature of sulfur-bearing carbonates," Litol. Polezn. Iskop., No. 4, 36-48 (1983).
4. I. S. Lazarev, "Geologic features of the structure and genesis of sulfur placers in the Gaurdak deposit," Fiz. Byull. GIGKhS, No. 1, 1-10 (1963).
5. B. V. Merlich and N. M. Datsenko, Formation Conditions of Sulfur Ores of Rozdol Deposit [in Russian], Vishcha Shkola, Lvov (1976).
6. Ya. K. Pisarchik and G. A. Rusetskaya, "Genesis of sulphur deposits of the Ciscarpathian region," in: Geochemistry and Mineralogy of Sulfur [in Russian], Nedra, Moscow (1972), pp. 120-131.
7. G. T. Sakseev, "Genesis of authigenic sulfur with special reference to the Zagaipol deposit," Litol. Polezn. Iskop., No. 6, 113-117 (1969).
8. A. S. Sokolov, "Patterns of the geological structure and distribution of sedimentary deposits of authigenic sulfur," Sov. Geol., No. 5, 80-103 (1958).
9. A. S. Sokolov, "Genesis of authigenic sulfur deposits," Litol. Polezn. Iskop., No. 2, 51-59 (1965).
10. A. S. Sokolov, "Genetic classification of authigenic sulfur deposits," in: Geochemistry and Mineralogy of Sulfur [in Russian], Nauka, Moscow (1972), pp. 40-55.
11. A. S. Sokolov, "Geologic and genetic studies of sulfur," in: Genesis of the Authigenic Sulfur Deposits and Exploration Prospects [in Russian], Nauka, Moscow (1974), pp. 10-30.
12. A. S. Sokolov and M. N. Zaitseva, "Characteristics of geological structure and types of sulfur ore of Rozdol deposit," Tr. GIGKhS, No. 4, 92-113 (1958).
13. Comparative Analysis of the Structures of Sulfur-Bearing Halogene Formations [in Russian], Nedra, Moscow (1981).
14. V. I. Kityk (ed.), The Structure and Distribution Patterns of Sulfur Deposits in the USSR [in Russian], Naukova Dumka, Kiev (1978).
15. N. P. Yushkin, Mineralogy and Paragenesis of Authigenic Sulfur in Exogenous Deposits [in Russian], Nauka, Leningrad (1968).
16. W. C. Gussow, Origin of Liquid Sulfur Deposits in the Earth's Crust [Russian translation], Vol. 7, No. 15, Nauka, Moscow (1984), pp. 261-262.
17. K. Pawlowska, "O gipsach, siarce rodziemej i pogipsowych skatach świetokrzyskiego miocenu," in: Ksisga pamiatkowa prof. V. Samsonowicza, Acta Geol. Pol., Warsaw (1962), pp. 69-82.

LITHOLOGIC FEATURES OF CARBONATE DEPOSITS OF THE EASTERN CASPIAN DEPRESSION IN CONJUNCTION WITH THEIR OIL AND GAS PROSPECTS

Yu. A. Ivanov and S. M. Blank

UDC 552.54:551.735(574.12)

Based on a lithologic-petrographic analysis, seven lithologic-facies zones are identified in Carboniferous rocks of the eastern Caspian depression. Three types of rocks forming the Carboniferous profile are distinguished, and the composition of the productive beds is specified. Hypotheses are advanced concerning the genetic processes responsible for the formation of the collector rocks, and conclusions are drawn concerning the geologic structure and paleogeography of the Carboniferous; recommendations are made on methods of oil and gas prospecting.

Deep drilling in the eastern Caspian depression discovered in the past few years Carboniferous carbonate rocks with commercial oil and gas prospects. The Carboniferous carbonates are characterized by complex lithologic-facies structure and significant variability of stratigraphic volume.

Exploration of Carboniferous carbonate sediments in the eastern parts of the depression led to the discovery of gas condensate-oil deposits at Zhanazhol and Urikhtau, the oil deposit at Kenkiyak, and oil and gas shows in the areas of Kozhasai, Aransai, Bozoba, and Eastern Tortkol (Fig. 1). The deposits are confined to two extensive oil and gas accumulation zones associated with regional synsedimentary subsalt rises — Yenbek (Temir) and Zharkamyss [2]. The productive horizons have been found in two carbonate strata: Upper Visean-Kashirian and Upper Moscovian-Upper Carboniferous.

Carboniferous carbonates in the eastern Caspian depression are underlain by sand-clay Lower Carboniferous and overlain by terrigenous Lower Permian (Assel-Arta) molasse formation. The stratigraphic division of the Carboniferous profile is based on determinations of foraminifers (Dobrokhotova, Dalmatskaya, Ganelina, Menyaeva, Beisenova, Solov'eva, and Sherbovich), brachiopods (Gubareva), and spores and pollen (Efremova, Poponina, and Taran).

The combined analysis of the data of deep drilling, seismic exploration, and lithologic-petrographic investigations have led the authors to identify in the Carboniferous seven zones with different lithologic-facies compositions and unequal stratigraphic completeness of profiles (see Fig. 1). We have determined the types of rocks forming the Carboniferous profile, described the composition of productive beds, and developed hypotheses concerning the genesis of collector beds, with new conclusions on lithology and paleogeography and suggestions concerning the oil and gas reconnaissance work. The lithologic zones are described in the sequence of data availability (from better studied to less studied units).

The most complete profile of the Carboniferous has been uncovered within the Zhanazhol-Sinelnikov section of the zone (zone I); two carbonate beds have been identified here: the Upper Visean-Kashirian and the Upper Moscovian-Upper Carboniferous, which are separated by a terrigenous bed of Podolsk horizon (Fig. 2a). The Lower Carboniferous is similar to contemporaneous rocks of lithologic zones II and III described below. The upper bed occurs only in this section and for that reason presents a special interest. Its subjacent layers are Podolsk sediments consisting of interstratified dark gray argillites, siltstone, and sandstone up to 400 m thick. The lower part consists of limestone with rare argillite, sometimes breccia interlayers; up the section, secondary dolomite is predominant.

The limestone of the Upper Moscovian substage in borehole 5 (Zhanazol, interval 3170-2900 m) is organogenic-lumpy, massive, and unclearly stratified recrystallized unequally porous matter. The bulk of the rock (from 50 to 80%) consists of granulated fragments of

All-Union Scientific-Research Institute of Oil Exploration Geology, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 91-102, May-June, 1986. Original article submitted January 18, 1985.

blue-green, less often purple, algae. Shells and detritus of foraminifers, echinoderms, brachiopods, bryozoans, gastropods, ostracods, and other organisms are present. The cemented microgranular carbonate material is dolomitized to variable degrees and recrystallized with the formation of medium-size and macroscopic grains; the grains are either distributed uniformly in the rock or form mosaic aggregates as spots and lenslets of a peculiar shape. Organogenic remains experienced recrystallization. At site 4, Zhanazhol, the Lower Carboniferous bed consists of dolomitized limestone. These are either dense rocks with scarce pores or heavily porous units. The pores are of an irregular, oval, sometimes slotlike, shape with broken edges, ranging in size from 0.1 to 0.25 mm. Many of the primary pores were apparently filled later with secondary calcite and dolomite, as some of the open cavities display the growth of crystals within the interstitial space. In some of the layers, the limestones are broken by numerous cracks that go in various directions, branch out, are sometimes interrupted, open, or filled with secondary dolomite. The cracks vary in width from 0.03 to 0.25 mm and up to 1 mm in swollen areas. In addition, microstylolite seams are present.

At the top of the Myachkov horizon, small-grained limestone replacement dolomites with faunal relicts are widespread (up to 100 m thick in site 4). The bulk of the rock (up to 90%) consists of mosaic dolomite aggregate with micrite relicts observed in its grains. The replacement dolomites are porous and cavernous; in some of the layers the pores and caverns, measuring up to 0.02–3.0 mm, penetrate the rock, endowing it with a spongy appearance. The pores are rounded, often with angular contours because of the epigenetic dolomite developed along their contours. The rock is heavily fissured. Dolomite rhombohedra are seen on the walls of some of the cracks. In individual layers the pores and cracks are partly or completely filled with bitumen.

The Upper Carboniferous in the Zhanazhol area is comprised of two strata: the lower, sulfate-carbonate bed and the upper, terrigenous bed. The lower bed consists of replacement dolomites, which are heavily porous, cavernous, and interstratified with microgranular relict-organogenic limestone and detritus. The replacement dolomite gives way up the section to anhydrite and anhydritic limestone. At the roof of the bed, organogenic-detritus-slurry anhydritized and dolomitized limestone is found. The sulfate-carbonate bed at site 5, Zhanazhol, is 272 m thick. The upper terrigenous bed consists of kaolinite-hydromicaceous argillites with sandstone and siltstone interlayers up to 164 m thick (site 5, Zhanazhol).

The upper gas condensate-oil Zhanazhol deposit is confined to the replacement dolomites of the top of the Moscovian stage and the Upper Carboniferous. The deposit is screened by Upper Carboniferous anhydrite and argillite.

In the southern continuation of the Zhanazhol-Sinelnikov zone, Tortkol zone (II) is identified, which contains no Upper Carboniferous or Bashkirian rocks. The Podolsk deposits here consist of carbonates, in contrast to the Zhanazhol zone.

The discovered profile of the Lower and Middle Visean consists of interstratified dark gray argillites with siltstone and sandstone of the uncovered thickness of 690 m (borehole P-1, Eastern Tortkol). Upper Visean and Serpukhovian limestone occurs on a terrigenous bed. At the bottom (300 m) of the carbonate profile, the limestone consists of microgranular calcite of a predominantly small-lumpy structure unequally enriched in granulated detritus of echinoderms, foraminifers, ostracods, and some unidentifiable remains. Up the section, light organogenic-lumpy algal and algal-foraminiferal limestone has been found with the detritus of echinoderms, brachiopods, crinoids, and bryozoans. The micrite cement is recrystallized to different degrees and dolomitized. The rock is dense, with no pores or cracks. The Upper Visean is 492 m thick, the Serpukhovian is 60 m thick.

The Moscovian sediments in the Tortkol zone consist of organogenic-lumpy limestone (thickness at P-1, 650 m). Dark gray to black organogenic-slurry spicular dolomitized limestone is present as separate layers, which mainly consist of recrystallized, sometimes sili-cified, carbonate sponge spicules. The micritic cement is slightly and finely dolomitized. The top (290 m) of the Moscovian consists of micro- and fine-crystalline limestone largely enriched in organogenic detritus. The rock is dense, with pores observed in microgranular carbonate mass and the internal cavities of organogenic remains.

North of the Zhanazhol-Sinelnikov zone, the Yenbek zone (III) is identified, which is confined to the Yenbek regional rise (see Figs. 1 and 2b). Within this zone, no Upper Carboniferous has been found, and the Moscovian is partly or completely absent. Under the Lower

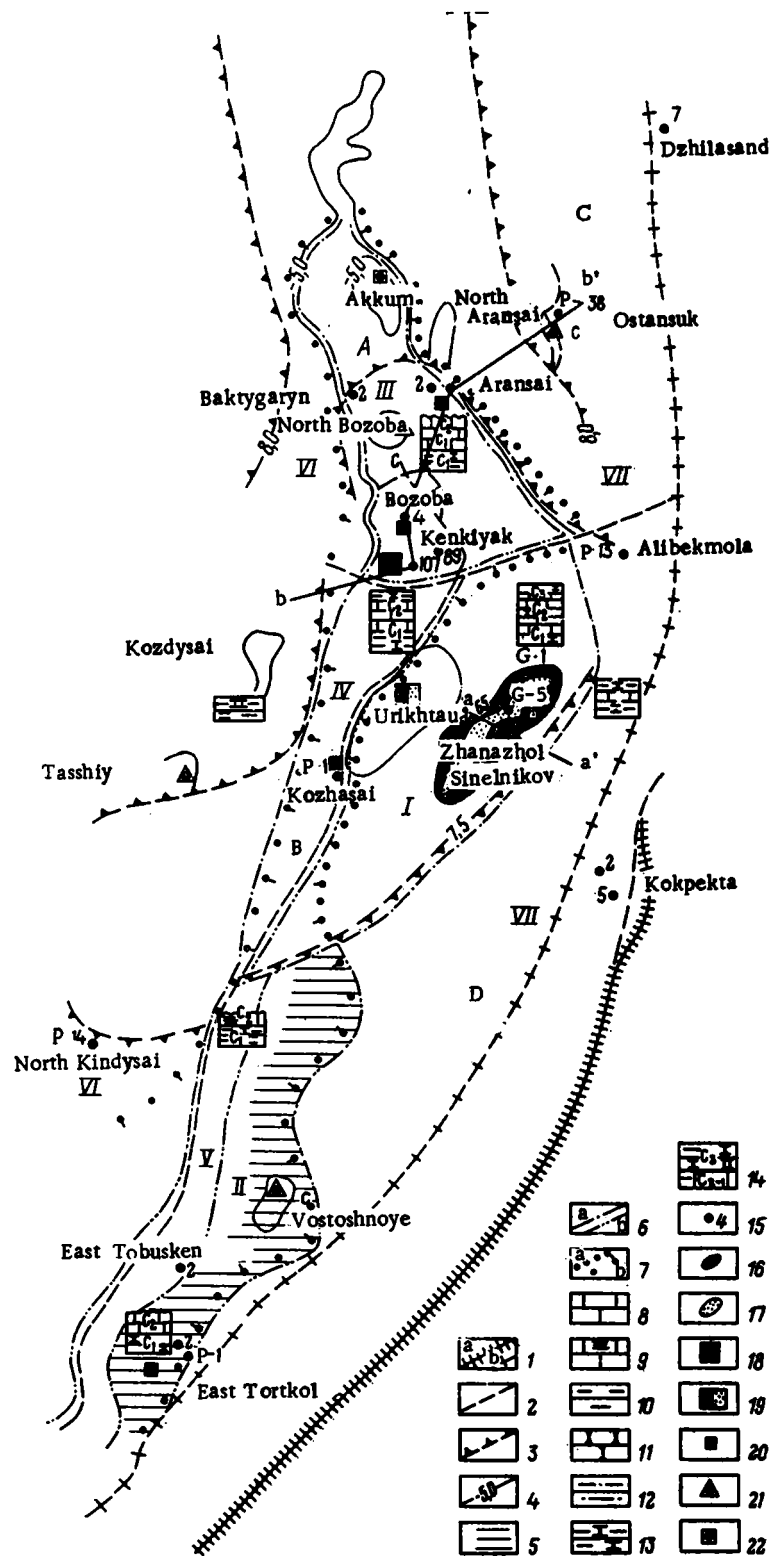


Fig. 1
(caption on p. 303)

Fig. 1. Lithologic zones of Carboniferous sediments (schematic): 1) faults (a - Sakmar-Kokpeta, b - Ashchisai regional fault); 2) rupture dislocations; 3) contours of large basement protrusions and the corresponding regional rises of the Carboniferous; 4) isohypses of the Carboniferous carbonate surface and contours of the rises on their roof; 5) buried Tobusken barlike rise on the reflecting horizon P₂ (hypothetically, Devonian roof); 6) boundaries of lithologic zones (a - determined, b - hypothetical); 7) boundaries of the wedging-out of Middle Carboniferous rocks (a - determined, b - hypothetical; bergstrichs pointing in the direction of wedging). Lithologic rock varieties; 8) limestone and dolomite; 9) limestone and dolomite with interlayers of terrigenous rocks; 10) argillite; 11) sandstone; 12) siltstone; 13) argillite with sandstone and siltstone interlayers; 14) column characterizing the composition and age of the Carboniferous of the lithologic zone; 15) deep borehole and its number; 16) oil deposit; 17) gas-condensate deposit; 18) area with proven pay oil deposits in the Carboniferous; 19) area with proven pay gas condensate deposit of the Carboniferous; 20) oil shows in Carboniferous sediments; 21-22) sites recommended for drilling (21 - parameteric holes, 22 - prospecting wells). Major tectonic elements: A) Yenbek barlike rise, B) Zharkamys arch, C) Ostansuk trough, D) Foremugodzhazhar trough. Lithologic zones: I) Zharnazhol-Sinel'nikov, II) Tortokol, III) Yenbek, IV) Kozhasai, V) Tobusken, VI) Kozdysai-North Kindysai, VII) Kokpeta-Ostansuk.

Permian terrigenous rocks, the drilling has uncovered different-aged Middle Carboniferous limestones: at site P-2, Aransai, Moscovian limestone; at site P-1, Aransai, Upper Bashkirian; and on Kenkiyak area, Lower Bashkirian rocks.

In borehole P-89, Kenkiyak, Oka-Serpukhovian organogenic-detrital and organogenic-lumpy limestones have been reached by drilling, which are oolitic and unequally cracked or porous at the bottom. The Oka-Serpukhovian sediments have not been penetrated by the drilling completely; the uncovered thickness is 274 m.

The Lower Bashkirian substage consists of organogenic-clastic and organogenic-detrital limestones, which consist mainly of ill-sorted heavily granulated shreds and nodules of algae and faunal fragments. Some of the limestone layers are oolitic and crystalline, and may be interstratified with dolomitized varieties that are porous and cavernous with stylolitic seams. In polished sections, some of the pores are seen to be confined to internal cavities of organogenic remains; there are also pores which are swellings in open cracks. The Lower Bashkirian is 154 m thick (site P-89). Productive oil beds (sites 106 and 107, Kenkiyak) are confined to organogenic-lumpy, mainly algal limestone of the top of the section. In the roof of the Lower Bashkirian, argillite of a kaolinite-hydromicaceous composition has been found. The Upper Bashkirian substage in borehole P-1, Aransai (interval 4834-4837 m), consists of massive organogenic-lumpy limestone, composed mainly of heavily granulated organogenic remains and shreds of algal tissue. The detritus is sometimes represented by anhydrite. In the roof of the section, conglomerate consisting of well-rounded phosphate fragments and less organogenic and micritic limestone cemented by brown phosphate and microgranular carbonate have been found at the boundary with the Lower Permian. P₂O₅ in the rock accounts for about 40%. The Bashkirian is up to 350 m thick (site P-2, Aransai).

The Moscovian (site P-2, Aransai), 258 m thick, consists at the bottom of organogenic-lumpy and organogenic-clastic limestone with microgranular calcite as the cement. The rock groundmass (up to 80%) consists of heavily granulated organogenic remains, among which blue-green algae, foraminifers, and other species can be identified. Pores from 0.03 to 0.25 mm are observed in the rock, which are confined to organogenic remains and the cement. The fracturation of the rock in polished sections and the data of well logging indicate that the rock is porous and fissured. According to the seismic data, the carbonate sediment thickness in this zone attains 1000 m and more (see Fig. 2b).

West of the Zhanazhol-Sinel'nikov zone is the Kozhasai zone (IV), where the bed of Carboniferous carbonate diminishes in thickness from 590 (site 3, Kozhasai) to 257 m (site P-1, Kozhasai); the Upper Carboniferous and the top of the Middle Carboniferous disappear in the profile. Carboniferous carbonates encompass a broad age interval from the Venevian horizon of the Upper Visean to the Kashirian horizon of the Moscovian stage inclusively (site 3, Kozhasai, interval 4035-3445 m); the rocks are light gray crystalline limestones with interlayers of black dense stratified argillites, which in some beds are finely interstratified with limestones.

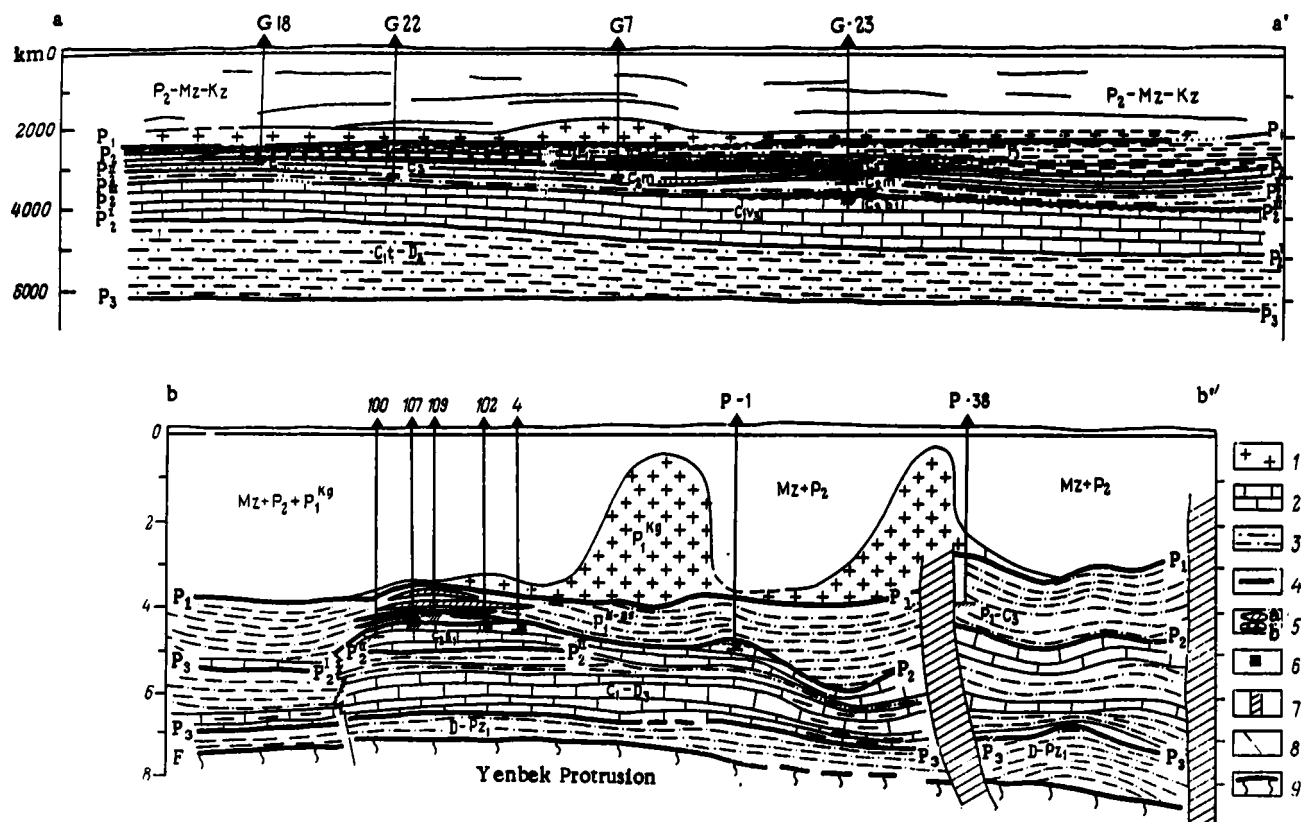


Fig. 2. Seismic geological profiles (see Fig. 1): a-a') across Zhanazhol deposit; b-b') along the line: Site P-38) Ostansuk-site 107, Kenkiyak. 1) Rock salt; 2) carbonate rocks; 3) terrigenous rocks; 4) seismicogeological boundaries; 5) deposits (a - Lower Permian oil; b - Carboniferous gas condensate); 6) oil shows in bore holes; 7) zones of loss of seismic correlation; 8) faults; 9) basement surface (refracting horizon F).

The southern continuation of zone IV is the Tobusken zone (V), where the carbonate bed thickness is reduced to 150 m (site 2, Eastern Tobusken); a considerable number of terrigenous interlayers appear in the carbonate beds. The Middle Carboniferous in this zone is represented by argillite and clayey dolomitized limestone. The Upper Carboniferous is absent in the profile, and the Lower Carboniferous is of a terrigenous composition; its uncovered thickness is 530 m (site 2, Eastern Tobusken).

Further west (according to seismic data), the Carboniferous consists mainly of terrigenous rocks (Kozdysai-North Kindysai zone, VI). The Carboniferous here has been reached by borehole P-2, Northern Kindysai, which discovered at 165 m the Upper Carboniferous gray microgranular calcareous sandstone, siltstone, and argillite with isolated clay limestone layers (see Figs. 1 and 2b).

East of the occurrence area of Carboniferous carbonates (zones I, II, and III) within Ostansuk and Foremugodzhazhar depression, Kokpektin-Ostansuk zone (VII) is situated; it has a carbonate-terrigenous composition and thicker Carboniferous beds (see Fig. 2b). The Lower Carboniferous in this zone can be judged by the data of borehole G-7, Dzhilansan, near the marginal seam, where sand-clay graywacke rocks of a Ural type have been found under the Kungur layers [3]. The carbonate-terrigenous composition and the large thickness of Upper, Middle, and Lower Carboniferous have been established on Kokpektin anticline within Foremugodzhazhar trough [4]. At site P-13, Alibekmola, where the hole was drilled in the saddle between the above-mentioned two depressions, Upper Carboniferous and Moscovian rocks more than 900 m thick have been uncovered. The lower portion of this profile (Vereyan, Kashirian, and partly Podolsk rocks) consists of gray limestone with argillite interlayers; the uncovered thickness is 258 m. Up the section, sand-argillite Podolsk bed, 362 m thick, has been identified. The Myachkov horizon and the Gzhelsk stage are of a terrigenous-carbonate composition; they are 280 and 92 m thick, respectively [5]. Somewhat east of site P-13, Alibekmola, near Emba, structural boreholes have uncovered Bashkirian stage and Vereyan (?),

Kashirian, and Podolsk horizons, composed of limestone, dolomite, argillite, and sandstone, sometimes variegated with abundant marine fauna [4].

The presence of coarse clastic graywacke rock varieties in the Carboniferous profiles of this zone suggest the proximity of erosion areas. They were geanticlinal rises, and toward the end of the Carboniferous became incipient orogenic structures of South Urals.

Each of these zones, outside the Sakmar-Kokpekta fault, which functions as the marginal seam, terrigenous graywackes, sometimes coarse-clastic Lower Carboniferous and Devonian rocks, are widespread. The intense dislocation of these sediments and the seismic data on deep parts of the profile suggest that these rocks are allochthonous.

The features of spatial distribution of lithologic-facies zones of the Carboniferous (see Fig. 1) in the eastern Caspian depression, offer a notion of the paleogeographic and paleotectonic settings during the Carboniferous. For the geological history of this region, the following should be borne in mind. This territory is confined to the southeastern margin of the Russian plate, which abutted the South Urals geosyncline in the east (along the Ural-Sakmar fault). In the outer trough of the geosyncline, "graywacke" (according to Yan-shin) terrigenous formation accumulated in the Early Carboniferous. During the Middle and Late Carboniferous flysch and carbonate-terrigenous formations developed there [8]. In the parts of the Caspian depression adjacent to the miogeosyncline in the Ostansuk and Foremogodzhar troughs, which were located on pericratonic subsiding marginal part of the platform, carbonate-terrigenous strata (zone VII) were formed. The larger thickness, flyschoid structure, and the presence of graywacke coarse-clastic rocks indicate that these sediments were transient from miogeosynclinal to platformal. Further west, subplatformal carbonate and terrigenous formations occur.

Lithologic zones I-IV, characterized by the common occurrence of thick (up to 1000 m) Carboniferous carbonate strata, are confined to regional rises — Yenbek, Zharkamyss, and the buried Tobusken bar.* Further south, the Carboniferous carbonates are traced within the south Emba Paleozoic rise and Karaton-Tengiz elevated zone. The Carboniferous marine basin within the contours of these synsedimentary rises offered relatively shallow-water conditions favorable for accumulation of organogenic and organogenic-clastic limestone.

Westward, the greater depths reduce the role of the carbonates in the profile, leading to a predominance of terrigenous sedimentation (zones V-VI). Fine clastic and well-sorted rocks in these zones mark them as distinct from zone VII.

During the Bashkirian and at the boundary between the Carboniferous and Permian, within the region of positive structures (Yenbek bar, Zharkamyss arch), ascending movements were observed which resulted in interruptions of sedimentation and erosions recorded in the disappearance of the Upper Carboniferous, part or all of the Moscovian, and some of the horizons of the Bashkirian and Lower Carboniferous in the sections of zones II-V [6].

The discovery of substantial oil and gas deposits in the Carboniferous carbonate rocks (Zhanazhol, Kenkiyak, and Urikhtal) is due primarily to the comparatively high capacity and filtrational characteristics of these rocks.

At the Zhanazhol deposit, the influx of oil from the Upper Moscovian-Upper Carboniferous attains 200-600 m³/sec and that of gas up to 200,000 m³/sec. The lithologic-petrographic investigations have determined that the upper gas condensate-oil deposit is confined to a particular type of rock: spongy dolomites (replacement dolomite). They form porous, cavernous-porous, and cavernous-fissured-porous collectors with a porosity (according to Bagrintseva) from 5 to 20% and more, and granular permeability from fractions of 1 to double-digit and triple-digit millidarcy. In some cases it is up to 2000 and 5400 mD. The fissure permeability attains 26.7 mD. The occurrence of the collectors is zonal: high-porous and permeable rocks in certain areas give way to varieties with poorer collector properties (sites G-1 and G-10). The substantial fluctuations of open porosity and permeability are due to uneven distribution of the void spaces and open cracks throughout the rock. Microscopic investigations of rocks showed that some of the rock specimens had up to 20-30% of the overall polished section area covered by interstitial space. The pores and caverns of "spongy" dolomites range in size from 0.1 to 3-5 mm. The voids of carbonate rocks are distinguished by irregular and variable shapes and combinations of pore channels, caverns, and

*The Tobusken bar is identified by the representing horizon P₃—hypothetically on the roof of the Devonian and during the Carboniferous it was a synsedimentary rise [7].

features, giving rise to diverse types of collectors ("complex" collectors) and significant variations of their parameters.

The collectors of Kenkiyak oil deposit in the Lower Bashkirian are limestones; they are organogenic-lumpy, organogenic-detrital, oolitic, cavernous, and fissured, with primary and secondary interstices ranging in size from 0.04 to 1.2 mm. Primary pores have been found in organic remains. In other cases, lixiviated areas of microgranular carbonate are observed. These pores have various shapes: rounded, irregular, angular, baylike, and webbed. The pore walls are covered by authigenic calcite or dolomite crystals. There are cracks, open or filled with calcite or bitumen. Open cracks are typically short, linear, branching, vertical, horizontal, or slanted with respect to the bedding. The cracks are often confined to stylolites. The suture jags are 0.5-0.25 mm high. The inner cavities are filled with black organic matter; pore and pore-crack collectors are widespread. According to laboratory tests, the porosity is not high (up to 6.3%); in polished sections it varies in a similar range (6-7%). The oil influx of up to 100 m³/sec from the Bashkirian, however, suggests that rocks with better collector properties must be present in the productive profile.

Interruptions in sedimentation, washouts, and related lixiviation, karsting, and fissuring of rocks have played an important role in forming the collectors of carbonate deposits. The pre-Permian erosion within the eastern margin of the Caspian depression was regional; it was most intense in the arches of synsedimentary rises. But there were washouts also at the boundary of the Lower and Middle Carboniferous and during the Bashkirian. In the arch of Yenbek rise, in view of the scale of the pre-Permian erosion, collectors with high capacity and filtration properties should be widespread. This conjecture is supported by the finds of friable limestone in borehole P-2, Aransai.

The formation of Zhanazhol collectors is associated with dolomitization processes. Judging by micrite relicts in replacement dolomites, the rock must have been a microgranular limestone, subsequently recrystallized. The calcite-to-dolomite conversion reduced the rock volume, which was accompanied by an increase in its porosity. As a result, the rock became "spongy."

The collector properties of productive beds are usually higher than in rocks of the same age and type devoid of hydrocarbons. Oil conserved the interstitial space and prevented the epigenetic alteration, such as the filling of cavities in carbonate rocks. There are no interstices or caverns in dolomites of site G-1, Zhanazhol, drilled outside the deposit.

Upper Carboniferous anhydrite was the cover bed of the carbonates of the upper deposit of Zhanazhol. The lower deposit is overlain by terrigenous Podolsk rocks. The Kenkiyak Bashkirian deposit is overlain by a terrigenous molasse formation of Assel-Arta age, which contains thick (up to 100 m) clay members and, according to Bakirov and Chimbulatov, possesses good screening properties [1].

The Carboniferous carbonate beds confined to synsedimentary positive structures form anticlinal oil and gas traps in the arch parts of Urikhtal, Zhanazhol-Sinel'nikov, and Yenbek rises (see Figs. 2a and b). Nonanticlinal traps associated with carbonates are also likely to be found: 1) stratigraphically screened traps (in the wedging-out zones of Middle and Upper Carboniferous); 2) lithologically screened and reef traps (on the boundary of terrigenous-for-carbonate substitution); and 3) tectonically screened (in the eastern part of the region along the Sakmar-Kokpekta and Ashchisai faults, where semiclosed structures are suggested by seismic data).

The study suggests a number of conclusions concerning the geological structure and paleogeography of the Carboniferous. On this basis, recommendations are made concerning the future exploration for oil and gas.

Carbonate Carboniferous sediments of the territory consist mainly of organogenic-lumpy and microgranular limestones and replacement dolomites. The former are mainly composed (60-80%) of granulated shreds of algal tissue, foraminifers, and diverse detritus, with reef-building organisms. The latter consist of microgranular calcite (up to 90%) unevenly enriched in granulated detritus of echinoderms, foraminifers, ostracods, and other microorganisms. The limestones are accumulations of a shallow-water sea basin with active hydrodynamics. Locally, the rocks have undergone substantial secondary alteration: recrystallization of the cement and organic remains, dolomitization, and sulfatization were the predominant processes. Metasomatic replacement occurred mainly to organic remains, while recrystallization encompassed cement and organic remains. Intensive dolomitization was

confined mainly to microgranular limestones (judging by preserved relicts), and among these to particular parts of the profile which had a primary porosity and permeability (the top of the Moscovian — the bottom of the Upper Carboniferous).

Some investigators believe that the Carboniferous carbonates of the eastern Caspian depression tend to repeat the ancient shoreline. We cannot agree with this view. The marine sedimentation settings extended much farther to the east of the territory under study, intruding into the Ural geosyncline. This is indicated by thick Carboniferous beds in the Foremugdzhar trough, the Berchogur and Bakai synclines, and other parts of South Urals. Therefore, there was no distinct stable coastline in the eastern Caspian depression during the Carboniferous. It appeared only in the Late Carboniferous and Early Permian, when Hercynian orogenic structures began to be formed in South Urals. Analysis has shown that the spread of Carboniferous carbonate sediments was controlled by regional rises — Yenbek, Zharkamyss, and Tobusken. Within these, there were relatively shallow-water portions of the sea basin, where favorable conditions were created for organogenic limestone beds to develop.

There is a view that carbonate bodies in the eastern Caspian depression are barrier reefs [9]. The material studied does not confirm the reef hypothesis of the limestone origin, because: a) no rocks of a calcareous framework consisting of reef-building organisms or coarse-clastic carbonate accumulations typical for the tail of the reef body have been found in the profile [7]; b) the organogenic material consists mainly of granulated shreds of algae, fragments of foraminiferal shells, and detritus; c) no sharp changes of the thickness of individual horizons are indicated by the available data; and d) stratification is seen in the profile with interlayers of dark argillite and silicite not typical for reef structures. The authors, however, do not rule out the possibility of future finds of reef structures within the Carboniferous carbonate beds.

The exponents of the reef theory of the Carboniferous carbonates interpret the stratigraphic interruptions in the Carboniferous profile as resulting from uncompensated deep-sea sedimentation outside the reef shelf. Zones II-V, where the Upper and partly Middle Carboniferous is missing, are confined to the arches of Zharkamyss and Yenbek rises. The shallow-water Middle Carboniferous limestone is overlain here by shallow-water molasse Assel-Arta deposit, giving no grounds to assume that the sediments during the latter half of the Middle Carboniferous and Late Carboniferous were accumulated in a depression. In view of the syndimentary nature of these rises, the stratigraphic disconformity at the Carboniferous/Permian boundary can be accounted for only by the existence of a substantial pre-Permian erosion. This view is confirmed by a find in the carbonate roof (site P-1, Aransai) of a conglomerate of phosphate and limestone fragments.

The carbonate complexes of the Upper Visean-Kashirian and Upper Moscovian-Upper Carboniferous are linked with the best oil and gas prospects in this territory, since their collector strata contain zonal covers (Podolsk and Upper Carboniferous) and regional covers (Lower Permian), as well as anticlinal and nonanticlinal traps. The replacement dolomites ("spongy" dolomites), widespread in the upper productive bed of the Zhanazhol deposit, exhibit the best collector properties. On the Kenkiyak area, the productive beds are confined to Lower Bashkirian organogenic-lumpy and algal-foraminiferal limestones which are lixiviated, porous, sometimes fissured. Interruptions in the sedimentation, erosion, and associated lixiviation karsting and fissuring of rocks, as well as dolomitization processes, contributed to the formation of the collectors of the two types.

Studies of the lithology and collector properties of Carboniferous carbonate rocks suggest that they are promising for the finds of oil and gas deposits in the zones with the maximum thickness of massive carbonate strata confined to the arches of syndimentary Zharkamyss and Yenbek rises; specific recommendations on drilling and geophysical exploration can be made on this basis.

The discovery of the Urikhtau deposit indicated the prospects of finding new deposits in arch of Zharkamyss rise (Fig. 1). On Urikhtau, Kozhasai, and Zhanatan areas, situated at the top of a large arch, exploration and prospecting should be concentrated. Judging by the wave field of the reflecting horizon P_2 , carbonates can be traced up to the Kozdisai and Ielemesaimrak areas. In order to determine the western boundary of carbonate occurrence, a parametric borehole 5500 m deep should be drilled in the Tasshiy area.

The Yenbek regional rise (zone III) in the roof of the Carboniferous carbonate is a large bar-shaped structure (along the isohypse -5 km, it is 75 × 25 km in size, with an

amplitude of 1-1.5 km). The arch part of the Yenbek bar is complicated by local elevations at depths of 4.2-4.8 km. On the Kenkiyak area, pay oil flows have been obtained from the carbonate complex. Small flows and signs of oil have been determined on Bozoba (site 4) and Aransai (sites P-1 and P-2). The Carboniferous on the Yenbek rise is thus oil-bearing everywhere. In view of the features of the deposits found in the carbonate beds on major regional structures (such as Astrakhan, Orenburg, and Karachaganak), one can expect a discovery of a unified extensive massive oil deposit within the Yenbek rise. Yet, the oil and gas prospects of the Carboniferous north of the Kenkiyak area have not yet been estimated.

In view of this, we recommend that geological exploration should be intensified on the Yenbek regional rise. Specifically, this will include: 1) locating on Severnaya Bozoba rise, a new parametric well of depth 5.5 km; 2) starting the first prospecting hole on the major rise at Akkum, prepared for drilling by seismic prospecting; 3) taking out of conservation and drilling to the planned bottom the 5-km hole 2 at Baktygaryn; and 4) continuing the area seismic exploration by the method of common deep points (MCDP) on Aransai, Northern Aransai, and west and south of these areas (covering approximately 20 × 20 km). This should be followed by drilling new holes to explore the oil and gas prospects of these territories. At present, a duplicate borehole for P-2 at Aransai could be drilled, since the latter could not be tested for engineering reasons.

In lithologic zone II, a parametric borehole should be drilled on Eastern rise (depth 5000 m, with the face in the Carboniferous); it is expected to uncover and clarify the oil and gas prospects of the Upper and Lower Carboniferous carbonate beds. MCDP exploration should be done on the southern continuation of Tortkol carbonate zone, so as to find new objects for oil and gas prospecting.

The Kokpekta-Ostansuk zone (VII) of the carbonate-terrigenous Carboniferous has not been studied sufficiently. An analysis of the geophysical data suggests that in the southern Ostansuk trough, thick carbonate beds may be present (high-velocity refractive horizon with $v_h = 5.4-6$ km/sec at the depth of 4.8-5.2 km). A parametric bore hole should be started, to be drilled to the depth of 5500 m, in the arch of Ostansuk Carboniferous fold. The oil and gas prospects of semiclosed structures adjacent to Ashchisaisk and Sakmar-Kokpekta faults should also be evaluated in this region, where tectonically and stratigraphically screened hydrocarbon deposits are likely to be found.

LITERATURE CITED

1. K. Kh. Bakirov, M. A. Chimbulatov, and A. V. Yakovlev, "The principal patterns of the distribution of oil and gas deposits in pre-Kungurian Permian beds of the eastern near-margin part of the Caspian depression," in: *The Formation of Oil and Gas Deposits in Deep Beds* [in Russian], Nauka, Moscow (1980), pp. 143-150.
2. E. S. Bulekbaev, Yu. A. Ivanov, and V. P. Smetanina, "Oil and gas prospects and directions of oil and gas prospecting in the eastern Caspian depression," *Geol. Nefti Gaza*, No. 12, 1-7 (1979).
3. I. B. Dal'yan and A. S. Posadskaya, *Geology and Oil and Gas Prospects of the Eastern Margin of the Caspian Depression* [in Russian], Nauka, Alma-Ata (1972).
4. L. V. Demchuk, Yu. A. Ivanov, and Yu. S. Shakhidzhanov, "The occurrence conditions of the Paleozoic in western Foremugodzhari region in connection with oil and gas prospects," *Novosti Neftyanoi i Gazovoi Tekhniki*, Ser. Geol., No. 6, 23-28 (1966).
5. A. K. Zamarev, *The Middle and Upper Paleozoic of the Eastern and Southeastern Margins of the Caspian Depression* [in Russian], Nedra, Leningrad (1970).
6. Yu. A. Ivanov, "The geological development of Caspian depression during the pre-Kungurian time in connection with oil and gas prospects," *Tr. Vses. N.-I. Geol. Neft. Int.*, No. 199, 28-41 (1977).
7. I. K. Korolyuk, M. V. Mikhailova, A. I. Ravikovich, et al., *Fossil Organogenic Structures, Reefs, the Methods of Their Study, and Their Oil and Gas Prospects* [in Russian], Nauka, Moscow (1975).
8. I. V. Khvorova, "Flysch and low molasse formation of the South Urals," *Tr. GIN AN SSSR*, No. 37, 352 (1967).
9. A. B. Chepelyugin and G. A. Sheremet'eva, "Reefogenic oil and gas traps in the south-eastern Caspian syncline," *Neftegazovaya Geol. Geofiz.*, No. 1, 3-7 (1978).

DIAGENESIS AND DOLOMITIZATION OF CARBONATE-SULFATE JURASSIC
AND CRETACEOUS IN DAGHESTAN

I. É. Éfendiev

UDC 552.14:552:53(470.67)

Based on a petrographic study, the features of diagenesis and dolomitization of carbonate-sulfate rocks of the Late Jurassic and Valanginian in Daghestan are described. Several diagenetic features have been identified which resulted in secondary alteration of sediments, dolomitization, and dedolomitization. A genetic interpretation of various types of dolomites is offered. The authigenesis of minerals and the patterns of mineral distribution in sections are investigated. Conclusions are drawn concerning the formation environments of sediments and the practical implications of secondary processes.

The set of sediments of the Upper Jurassic and Cretaceous studied in this paper holds a special place amid the diverse sedimentary rocks of Daghestan. These sediments exhibit a broad variety of occurrence patterns and development closely linked with the facies-paleogeographic and hydrochemical conditions of their formation.

The chemical-mineral composition and the structural and textural characteristics of these rocks determine their uses in the economy, making their study important from a practical as well as scientific point of view.

Although these rocks have been studied by a large number of investigators who espoused different theories [1-3, 5-9, 15, 17], the diagenetic features and dolomitization of these units have remained obscure until now.

We have investigated these rocks in reference sections (Fig. 1), collecting a large number of specimens of various rock types. These samples were subjected to comprehensive investigation, although the petrographic studies were most detailed, because this method offers best information on diagenesis and dolomitization.

By the lithologic composition, the carbonate-sulfate formation of the Upper Jurassic and Valanginian is subdivided into three beds: the lower limestone-dolomite bed, the middle gypsum-dolomite bed, and the upper limestone-dolomite bed [7]. The formation consists of limestone, dolomite, gypsum, and anhydrite, with rare clay siltstone and sandstone interlayers in South and Northeast (flatland) Daghestan, and lenses and inclusions of brecciated carbonate rocks in Central and Northwest Daghestan. In some of the profiles (at Karata, Gergebil, Gapshima, Krasnyi Most, Arakamy, etc.), the bottom of the Upper Callovian-Oxfordian exhibits silicic units (nodules, lenses, concretations, geodes, etc.) distributed unevenly through this profile along the course, with a tendency for bed-conjugated occurrence.

The results of the study suggested that the diagenetic processes made a major contribution to the transformation of the sediments and were responsible for the formation of various authigenic minerals, determining their structure and texture. In particular, minerals such as calcite, dolomite, gypsum, anhydrite, barite, celestite, sulfur, siderite, glauconite, pyrite, limonite, hematite, opal, chalcedony, quartz, etc., have been found in the rocks. Structurally and texturally, the following rock types have been described: pelitomorphous-massive, pelitomorphous-lumpy (oolitoid), pelitomorphous-crystalline-augen, pelitomorphous-organogenic-oolitic, organogenic-oolitic, oolitic, and crystalline-granular. By the size of the grains [11], the rocks are subdivided into coarse-grained (>1 mm), large-grained (1-0.5 mm), medium-grained (0.5-0.1 mm), small-grained (0.1-0.01 mm), and pelitomorphous (<0.01 mm). The first two varieties of textures are extremely rare among the rocks studied.

Institute of Geology, Daghestan Branch, Academy of Sciences of the USSR, Makhachkala.
Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 103-115, May-June, 1986. Original article submitted October 30, 1984.

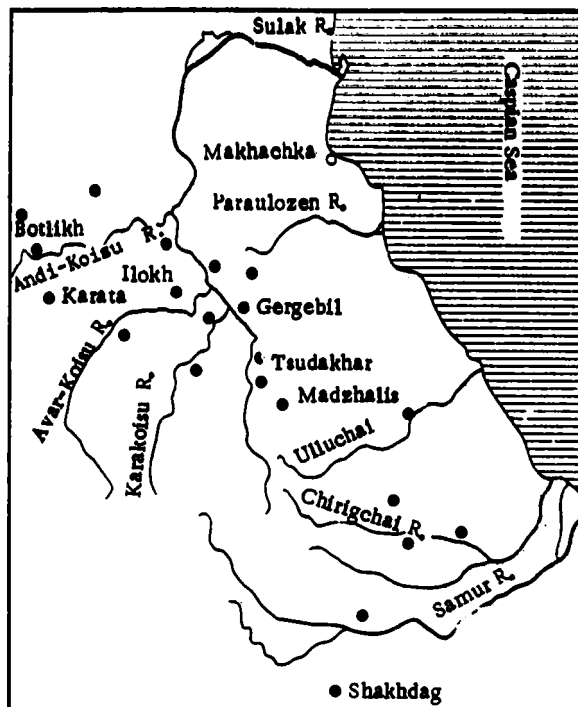


Fig. 1. Schematic map of the region studied.
Dots indicate the sites of reference profiles.

The lower limestone-dolomite bed (the Upper Callovian-Oxfordian) consists of limestone, dolomite, and rock varieties intermediate between the two.

In the profile near Untsukul, these are, according to microscopy, medium- and fine-grained limestone containing poorly preserved similar foraminiferal species resembling very fine-grained pelite lumps ridden with burrows of ooze-living organisms. The lumps are surrounded by cementing carbonate mass, slightly affected by initial dolomitization.

The large caverns formed by lixiviation, dissolution, and erosion of substantial amounts of calcite, gypsum, and organic remains during the early diagenesis of sedimentary rocks exhibit distinctly, along the contours, dolomite rhombohedra up to 0.03 mm in size or smaller, which, we believe, precipitated directly from high-magnesium solutions during the diagenesis. The caverns also contain barite, celestite, micro- and monocrystalline calcite, hematite, limonite, and other authigenic minerals. The form of occurrence and segregation sequence of these minerals in caverns and the cracks crossing these caverns indicate the stadial processes which resulted in sediment alteration, which can be interpreted as follows.

The dolomite rhombohedra are nonuniform and consist of cores and shells. While the cores are composed of fine-grained calcite, their outer contour is represented by two or three rims of generation of pure dolomites of different interferences, sometimes opaque, as revealed by their distinct lamination. After them, small- and medium-grained calcite was deposited, which toward the middle of the cavern became monocrystalline. Sometimes the latter is replaced on the contour by barite; sometimes it occupies areas between dolomite grains functioning as a cement. In the cracks crossing these caverns, mainly medium-grained calcite and sometimes crystals of mosaic dolomite with no overgrowth signs are observed. The following mineral segregation sequence can thus be assumed: 1) diagenetic dolomite, calcite, and barite; and 2) epigenetic (catagenetic) calcite and dolomite, which were formed in cracks.

A different specimen (Fig. 2a) collected somewhat lower down the profile consists of fine-grained limestone with small (0.045 mm) authigenic quartz particles with stylolitic seams scattered through the rock groundmass. The seams frequently observed in the rocks under study are thicker at the bends. At the "bottoms" of these bends, quartz micrograins are concentrated, which apparently were brought here by solutions flowing from fractured zones along the cracks associated with stylolites as a result of the dissolution of carbonate

mass. These grains are elongate or lenticular, with their major axes oriented mainly along the fluid course. In narrow vertical channels of the seam, no such grain accumulations are usually observed, apparently reflecting the different liquid velocities in the different cross sections which made the conditions unfavorable for accumulation of the grains in these parts of the seam (no traps). This distribution of terrigenous-colloid matter at the lower parts of the bends of stylolitic seams can be used as an indicator in diagnosis for identifying the upper and lower surfaces of a bed, which is crucial for determining the normal or reverse occurrence of a layer.

At the Mogokh bridge, the profile of this bed consists of medium-grained dolomite and organogenic-oolitic limestone containing large quantities of well-sorted terrigenous matter consisting of quartzose and feldspathic grains, clastic quartzite, clayey schists of angular or angular-rounded shape, and of sand-grain size, distributed in the carbonate mass with no regular orientation.

Carbonate and silicic matter, represented by calcite and opal, is the cement. The feldspar is pyritized. The fissured grains of bright green glauconite present in the rock indicate the authigenic origin of the feldspar and the diagenetic origin of the cracks; otherwise, fissured glauconite would not be transported here as unfractured whole grains. Dolomite is found here as well-faced rhombi and crystals of a tabellar habit with incised edges. Dolomite is formed sometimes after opal and chalcedony.

Slightly higher in the profile is organogenic limestone, consisting of intact microorganisms and their fragments, lumpy calcareous units, and oolites, up to 0.3 mm, with quartz grain nuclei. Chambers of large organisms are sometimes filled partly with dark green glauconite or orange-red iron hydroxides formed by direct internal chemical precipitation.

All these data suggest that the sediments were accumulated in a littoral or shallow-water part of the basin in a hydrodynamically active environment. Terrigenous matter was brought into the basin from outside, and the erosion area was at some distance from the site of deposition.

The cooccurrence of differently aged minerals (dolomite, iron hydroxides, and glauconite) in sediments suggests the possible formation of dolomite in an acidulous, nearly neutral environments of an alkaline medium with pH 6.8-8. According to Teodorovich [13], primary dolomite can be formed at various alkaline pH values, although he believes the most typical setting to have a pH of 8.1-8.8.

Chilingar et al. [16] believe that syngenetic dolomites are formed at pH 8.

A photograph of the specimen from this profile (see Fig. 2b) shows a cavern filled with opal, chalcedony, and quartz in the left part; the chalcedony is partly replaced with calcite. The observations of the forms of recent finds of opal, chalcedony, and quartz in caverns by Depples [4] suggested that phanocrystalline quartz is found mainly in central parts of cavities, while their periphery is covered, from the center toward the rock, by chalcedony and opal in this order. This distribution of silicic minerals is a result of stadal alteration of matter. Originally, the precipitated silica in the form of gel is transformed into opal, which ages in these conditions. As a result, crystallization begins from the central parts of an opal unit with the transition through a chalcedony phase into quartz. The process is slow and develops gradually from the central part toward the perimeter. Eventually, the cavity becomes filled with quartz with an ordered crystalline structure. Authigenic quartz in cavities, sometimes large (larger than the microscope's field of view as a factor of 1-1.5), found by us in some of the profiles of the Upper Jurassic carbonate-sulfate complex (Mogokh, Kullibukhnamakhi, Sardarkent, and other areas) was obviously formed by this route rather than direct precipitation from silica-oversaturated solutions. This process, however, is observed in a natural environment: for example, precipitation of quartz as rims growing on clastic grains and remains of silicic organisms, the formation of authigenic dispersed quartz as insets in carbonate mass of rocks (Untsukul), etc.

Dolomite was isolated in caverns and more permeable areas around the caverns as well-faceted clear rhombohedra of a larger size. Outside these zones, dolomite crystals are tabular and smaller, with calcite cores and secondary dolomite outer rims. The dolomite crystals in these parts of the rock develop as a result of grain growth with a very dense packing and granoblastic texture. Red and orange-brown iron hydroxides occurring in abundance in the rock as large globular forms have authigenic quartz cores, which became the centers in which the globules germinated.

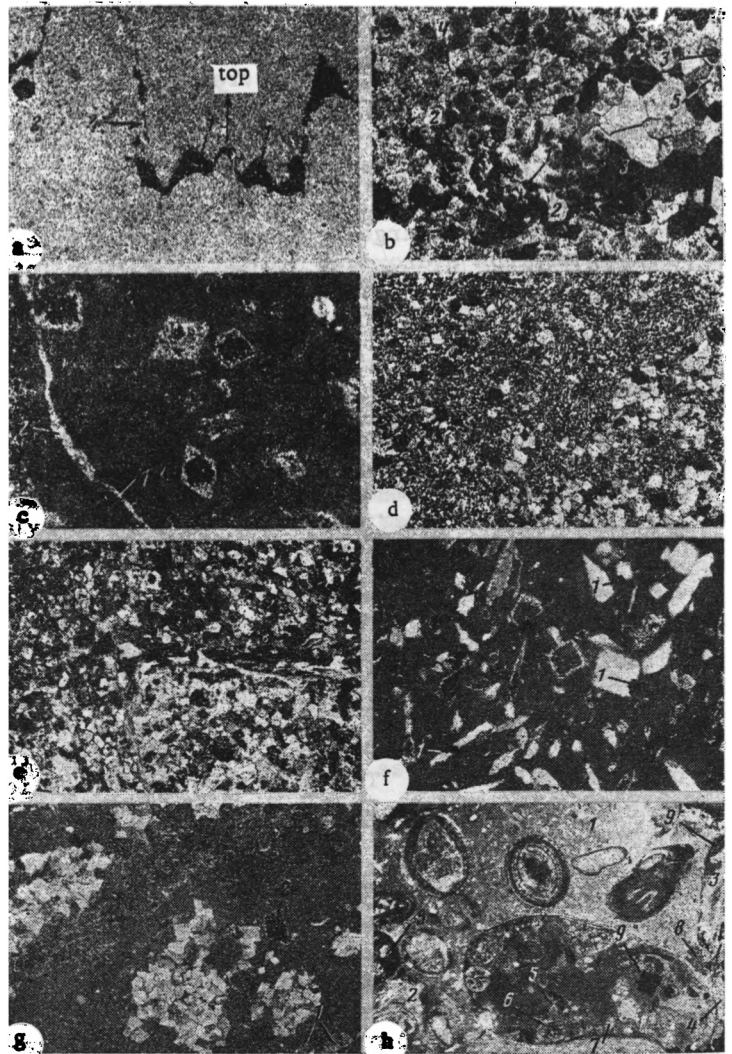


Fig. 2. Diagenetic features of carbonate-sulfate rocks. a) fine-grained limestone with microstylolites; black small point insets are limonite, white and gray small grains in the groundmass and in the bends of stylolitic seam are quartz (1), fibrous calcite (2); black stylolite background is iron hydroxide; Upper Jurassic, Upper Callovian-Oxfordian, Untsukul, specimen 41, polished section, crossed nicols, magnification 45×; b) medium-grained densely packed dolomite with caverns filled with opal (1), chalcedony (2), idiomorphous quartz grains resulting from chalcedony recrystallization (3), calcite (4), and iron hydroxides (5); Upper Jurassic, Upper-Callovian-Oxfordian, Mogokh bridge, specimen 7, polished section, crossed nicols, magnification 45×; c) pelitomorphous dolomitized limestone with rare foraminiferal remains. Visible are dolomite microrhombi with dissolved inner portions, indicating dedolomitization of limestone; fissured dolomite (1) and calcite (2) were formed, possibly during epigenesis, later than syngenetic rhombidolomite; Upper Jurassic, Upper Callovian-Oxfordian, Karadakh, specimen 101, polished section, crossed nicols, magnification 45×; d) fine-grained gypsum, intensely dolomitized, Upper Jurassic, Kimmeridgian-Tithonian, Karadakh, specimen 99, polished section, crossed nicols, magnification 45×; e) dolomitized clay-silt limestone with silicic-clay cement and opal nuclei of dolomite rhombohedra; the transition of fibrous chalcedony to fibrous calcite and dolomite formation after calcite is visible. Upper Jurassic, Tithonian, Sardarkent, specimen 191, polished section, crossed nicols, magnification 45×; f) pelitomorphous dolomitized celestite-bearing, locally clayey limestone. Isometric formations of iron oxides (1) can be seen on celestite grains: Lower Cretaceous, Valanginian, Kullibukhnamakhi, specimen 141, polished section, crossed nicols, magnification 45×; g) another field of the polished section of specimen 141; dolomite crystals are seen to be confined to rock areas where the clay fraction is present which has a sharp contrast with the carbonate groundmass; celestite grains (1) and celestite rhombohedra in the position of full extinction (2). Crossed nicols, magnification 45×; h) organogenic-clastic oolitic limestone; groundmass with crystallized areas is seen containing inequigranular calcite [monocrystalline (1), fibrous (2), medium-grained (3), and small-grained (4)], quartz (5), chalcedony (6), chalcedony being transformed into quartz (7), barite substituted by calcite along contour (8), and brown iron oxides (9). At the bottom of the photograph, a large lump is seen, which consists of the same material as the main carbonate substrate. It is a nodular formation — pseudo-conglomerate — with clastogenic grains of quartz, silicic rocks, and oolites, including sideritic ones, with nuclei formed of the above-mentioned fragments and iron oxides. Lower Cretaceous, Valanginian (?), specimen 179, crossed nicols, magnification 17×.

Types of dolomite crystals are thus distinguished, revealing the formation features of two stages. During the first stage (syngenetic-diagenetic), a dolomite sediment was formed and converted into isometric-tabular dolomite crystals. Authigenic quartz and globular forms of iron were segregated. During the second (diagenetic) stage of dolomitization, peripheral rings grew on dolomite grains.

The lower part of the profile near Karadakh, corresponding to the Upper Callovian-Oxfordian, consists mainly of limestone, sometimes heavily dolomitized. Dolomite in these rocks is represented by large rhombic crystals, up to 0.48 mm across, with sharp and distinct crystallographic boundaries and no overgrowth rims. Weathered varieties and major accumulations of dolomite crystals confined to various parts of carbonate groundmass are found. Noteworthy, the cracks crossing the dolomite rhombohedra are filled with dolomite of a different optical orientation, indicating its secondary origin.

The study of a different sample from underlying layers (see Fig. 2c) indicated that dolomite was segregated here as well-faceted large rhombi (0.57×0.375 mm); in small quantities (not more than 8-10 rhombi within the microscope's field of view) they are dispersed in calcitic groundmass. The rhombi have outer boundaries appearing as light "frames," which are not optically oriented and contain microgranular dolomite. Almost all of the rhombohedra and other shapes of dolomite crystals are lixiviated in the middle. This indicates that lixiviation of dolomite crystals begins at the center, where the crystal was first originated. This inverse process can be described as dedolomitization of carbonate rocks.

The dedolomitization was also observed by us in carbonate-sulfate rocks in several profiles (at Tlokh, Karata, and other sites). It is most widespread and typical for gypsum-dolomitic beds of Central and Northwest Daghestan, probably associated with intense lixiviation of sediments in this region.

The gypsum dolomitic bed (Kimmeridgian-Tithonian) consists of alternating plates and lenticular bodies of gypsum and anhydrite varying in thickness from 0.5-2 to 15-20 m, limestone, dolomite, and limestone-dolomitic breccia, sometimes with scarce interlayers of schist clays and siltstone.

Near Mogokh bridge at the base of gypsum-dolomite bed, pelitomorphous limestone is observed with a small admixture of clay matter. Up the profile, two gypsum beds are seen separated by a 15-m-thick dolomite layer. The microscopic investigation showed that the gypsum of these two beds are different in texture. The gypsum of the lower bed is small-crystalline, fine-grained, and slightly calcareous. The crystals are of a unidirectional optical orientation, suggesting that the gypsum was deposited in hydrodynamically stagnant lagoon zones. It contains single fresh grains of quartz of a wavy extinction, small amounts of pelitic material, and iron sulfides in the form of "soot" pyrite. The gypsum of the top layer is similar in crystal properties, but the optical orientation of crystals, signs of calcitization, and terrigenous admixture are absent; the gypsum is heavily cavernous and fissured; it is pink. The lixiviation caverns are partly filled with granular pyrite, slightly oxidized in the middle, with gradual transition to brown iron oxides.

The formation settings of these two gypsum varieties were slightly different, although they were formed with a short interval in time. During the time of accumulation of the lower gypsum bed, the settings in which the subjacent limestone were deposited were probably still preserved, and substantial quantities of terrigenous material continued to be brought into the basin and deposited, along with evaporites, in a calm hydrodynamic environment of the water basin.

During the accumulation of the upper layer, the influx of terrigenous matter was reduced, the basin became less quiet, and the sedimentation of gypsum took place. The intense pyritization of gypsum suggests a reducing environment of sedimentation. Later, the diagenetic processes partly or completely oxidized pyrite, with transition to brown iron oxides, and eventually the formation of pink gypsum.

A study of the diagenetic features of carbonate rocks near Karadakh, south of the above-described profile, shows that dolomite was formed here by replacing the main limestone mass with subsequent recrystallization and development of large idiomorphous crystals with overgrowth rims confined mainly to high-porosity and filtration zones.

These rocks are cemented with silicic-carbonate material, mainly opal, calcite, and less often barite. In pores and cavities, the latter were replaced by dolomites occurring as iso-

lated individuals within calcite monocrystals. This form of dolomite segregation can be viewed as one of the formation routes which probably involved a redistribution of matter within the calcite crystal rather than magnesium influx from the surroundings.

Dolomite originally could have precipitated directly from the solution during the sedimentogenesis as fine dolomitic residue, later, during the diagenesis it was redistributed, leading to metasomatic replacement of sediment rock and formation of augen-spotty texture typical for the rocks in this bed.

The gypsum in the profile is heavily dolomitized (see Fig. 2d). The photograph shows gypsum saturated with dolomite crystals which are rhomboid or slightly rounded at corners, so the crystals have an isometric tabular shape. The crystals are almost of the same size (0.1 mm); they are clear, with no nuclei or rims, and evenly distributed in the rock, indicating a syngenetic dolomite formation. The clear large chiplike celestite crystals with cut ends found in these gypsums are oriented in the same direction and encrusted with gypsum crystals.

The next profile where we studied the sediments is located near Tlokh Village. Gypsum is widespread here, with a total thickness of 125 m within a 300-m-thick bed. Gypsum is interstratified with dolomite and dolomitized limestone. Pure limestone is virtually absent. Gypsum in this area is partly dolomitized. Dolomite is present as well-crystallized clear rhombohedra with no secondary alteration, measuring 0.06-0.075 mm. Rhombic dolomite crystals, preferably situated along the long diagonal perpendicular to gypsum bedding or cleavage, are found sometimes, probably indicative of the sediment structures. Calcite microcrystals are also observed along cleavage planes.

The Karata profile, situated 20 km southwest of the above profile, exhibits gypsums in interstratification with dolomite and dolomitized limestone as 0.5-20 m thick beds. The gypsums are white, dull, or pink, and consist of small or large crystals. In contrast to Tlokh gypsum, these rocks are heavily pyritized and ferruginated, with poor calcitization and dolomitization.

The dolomitization is uneven, with dolomite rhombi confined mainly to porous or permeable segments or found along cracks as chains or small accumulations, indicating a diagenetic origin of the dolomite.

The principal cementing fillers of carbonate rocks are opal, calcite, barite, and sometimes gypsum. The replacement of gypsum and baritic cement in interstitial space is accompanied by the formation of idiomorphous dolomite crystals. A characteristic feature of the rocks is ubiquitous, sometimes intense, ferrugination, as well as an increase in the quantity of terrigenous matter up the section, silicification of rocks, and a reduction of pyritic material (sulfidization) of gypsum in this direction, concurrent with increase of dolomite content.

Detailed observations of the diagenetic characteristics of rocks of the gypsum-dolomite bed generally suggest that dolomitization of these rocks was syngenetic-diagenetic; dolomitic material precipitated from magnesium-saturated solution during sedimentogenesis in a deep lagoon setting (Central and Northwestern Daghestan) and later during early diagenesis was redistributed and gave rise to syngenetic-diagenetic dolomite. We believe that this is confirmed by burrows of ooze-living animals; these are filled with fine opaque material, which is the product of sediment processing by burrowing organisms. The sediment has not been affected by dolomitization. This may be evidence of the possibility of life of organisms during early diagenesis after the sediment was dolomitized.

The syngenetic-diagenetic transformation of the sediment is suggested also by a rock specimen collected from the same bed (Tithonian) near Sardarkent in South Daghestan (Fig. 2e). In the photograph, it is seen to consist of silt-clay medium-grained dolomitized limestone. A progressive replacement of fibrous chalcedony by fibrous calcite is clearly seen. White dolomite rhombohedra have opal cores (black points at the crystal center); those without a core are quartz grains. Dolomitization took place during sedimentogenesis. When silica precipitated as opal, it became the germination center of rhombic dolomite crystals and provided matter filling the interstices. The conversion of chalcedony to calcite occurred during diagenesis.

The upper limestone-dolomite bed (referred by us to Valanginian) crowns the carbonate-sulfate profile of the Upper Jurassic in Daghestan. Valanginian rocks consist of organogenic-clastic, oolitic, oolitoid, and partly celestite-bearing dolomitized limestones, and in northwestern areas also gypsum.

TABLE 1. Diagenetic Features and Types of Dolomitization of the Carbonates in Upper Jurassic and Cretaceous Rocks

Daghestan area	Age	Diagenetic features																	Dolomitization types			
		compaction	loosening	concretion formation	oolite formation	nodule formation	drying cracks	stylolitic seams	ferrugination	reduction	cementing	crystallization	recrystallization	dissolution	lixivation	corrosion	cracks	growth	authigenic mineral formation	syngenetic	syngenetic-diagenetic with superimposed (secondary) dolomitization	epigenetic (catagenetic)
Northwestern	Valanginian	+	—	—	—	—	—	—	+	—	+	—	+	+	—	+	+	+	B, C, O, P, Q	—	+	—
	Kimmeridgian—Tithonian	+	+	—	+	—	—	+	+	+	+	+	+	+	+	+	—	+	B, Cl, C, O, Q, P	+	+	+
	Upper Cretaceous—Oxfordian	+	—	+	—	—	+	+	+	—	+	+	+	+	+	+	+	+	B, Cl, C, O, G, Q	—	+	+(?)
Central	Valanginian	+	+	—	+	—	—	+	+	+	+	+	—	+	+	+	—	—	B, Cl, S, O, Q	+	+	+
	Kimmeridgian—Tithonian	+	—	—	+	—	—	+	+	+	+	+	+	+	—	—	+	—	B, Cl, C, O, G, Q	+	+	+
	Upper Cretaceous—Oxfordian	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	—	B, Cl, C, O, G, Q	+	+	+
Southern	Valanginian	+	+	—	+	+	+	—	+	+	+	—	+	—	+	+	+	+	B, Cl, C, O, G, Q	+	+	—
	Tithonian	+	—	—	—	—	+	—	+	+	+	+	—	—	+	—	+	+	B, C, O, Q, P	—	+	—

Note. Plus indicates the presence of the diagenetic feature and dolomitization type; minus indicates their absence. Notations: B) barite, C) celestite, Cl) chalcedony, O) opal, Q) quartz, P) pyrite, G) glauconite, S) siderite. Calcite and dolomite are not indicated because they are the rock-forming minerals.

The photograph of a polished section (see Fig. 2f) shows clearly chiplike angular large celestite crystals, sometimes with good crystallographic facets, and dolomite rhombohedra. A different field of view of the same polished section (see Fig. 2g) shows clearly that dolomite crystals are confined to areas where clay matter is predominant. The claying of rocks is nonuniform; the clay is distributed in the carbonate mass along fissured zones in the form of lenses, veinlets, pockets, and amorphous local strips and spots.

The predominant distribution of dolomite crystals in the limestone claying areas clashes with the literary data [16], suggesting that the presence of clay minerals in limestones may delay dolomitization of the sediment. The issue remains unresolved and requires further investigation.

Studies of the rock samples from the Valanginian near Madzhalis (see Fig. 2i) show that these rocks are represented by organogenic-clastic oolitic limestone with a broad spectrum of bioclastic fragments of diverse shapes and sizes. The cementing basal groundmass consists of pelitomorphic carbonate, locally recrystallized into inequigranular calcite.

At the bottom of the polished section photograph, a large lump is seen which consists of the same matter as the main carbonate substrate. It is a nodular early diagenetic formation reminiscent of conglomerate. It contains clastogenic grains of quartz, silicic rocks, and oolites, including siderite individuals, with nuclei consisting of the above-mentioned fragments and iron oxides. The nodule was formed in a submarine environment as a result of periodic rolling on the seafloor.

Almost all clastic grains and oolites contained in the nodule are situated along its outer contour. Oolites in the nodule clearly have fewer concentric rings and are much smaller (up to 0.3 mm), while the oolites in the groundmass (outside the nodule) measure up to 0.75 mm or more across and contain more concentric layers, suggesting that the oolite stopped growing after it was trapped in the nodule mass.

The detailed petrographic investigations of carbonate-sulfate rocks provide a notion of the diagenetic transformations which took place during the Upper Jurassic-Valanginian in Daghestan territory. These transformations were caused by physicochemical, biochemical, and physical processes and the influx and erosion of material which altered the sediments in the interval between accumulation and lithification. Subsequent alteration of the lithified sediment rocks belongs to epigenesis (catagenesis) and metamorphism.

Stadial alterations of sediments have been linked with extensive manifestations of diagenesis. Chilingar et al. [16], citing Krumbein, mention the published descriptions of some 30 diagenetic processes causing alteration of the mineral composition, influx and loss of material, and alteration of structures and textures up to complete disappearance of the pre-existing traits. According to these views, the stadial alterations of the sediment rocks are due to gradual transitions which overlap in time and space, making it extremely difficult to draw distinct boundaries. Despite this, our study of these rocks has revealed and identified among the factors controlling sedimentogenesis the diagenesis and epigenesis, those features which are classified as diagenetic (see Table 1).

Depending on the degree of crystallization associated with the grain growth, we have subdivided carbonate rocks into five groups: 1) nonrecrystallized; 2) slightly recrystallized; 3) moderately recrystallized; 4) heavily recrystallized; 5) completely recrystallized.

The occurrence of these groups on the territory of Daghestan varies, and they are distributed as follows.

The first group are pelitomorphic and organogenic-clastic limestone varieties found mainly in the profiles of Krasnyi Most, Karadakh, Tlokh (the bottom of the gypsum bed), Gapshima, and Sardarkent. This is the least widespread rock group.

The second group, in addition to the above profiles, is present also at Kullibukhnamakhi, Karata (the bottom of the gypsum-dolomite bed), and near Madzhalis.

The third group includes carbonate rocks developed partly in the lower half of the gypsum-dolomite bed and the lower limestone-dolomite bed near Untsukul', Tsudakhar, Gapshima, Karata (gypsum-dolomite bed), and Sardarkent (Tithonain). This is the most widespread rock group in Daghestan's territory.

The fourth group has a limited occurrence and is traceable as a narrow strip stretching submeridionally from the Gimra Ridge to Les Ridge syncline; in this zone a number of depos-

its of so-called marmorized limestone have been described in Tsudkhar and Kutisha profiles, and within Kadark anticline, at Pereval'noe, Rodnikovoe, etc. In addition, this group includes certain rock varieties observed at Untsukul', Mogokh Bridge (extremely rare), Krasnyi Most, and near Karadakh and Chokh.

The fifth group is extremely rare and has a highly limited occurrence. These rocks are found in thin (0.3-0.5 m) layers in some areas of Central Daghestan (Chudakhar, Mogokh, etc.).

Dolomitization of Carbonate-Sulfate Rocks. The theory of dolomite formation has been developed in depth and substantiated by Soviet and foreign investigators [10, 12-14, 16, etc.].

According to Strakhov [10], dolomites are not formed currently in marine environments; they are formed in two types of lakes: sodium lakes (Tanatar lakes) and coal-magnesium lakes (Balkhash, lakes of the Burlin group, and Great Salt Lake in the United States). He also demonstrated that dolomite could be formed in marine conditions in the geological past in the presence of the necessary concentrations of calcium and magnesium carbonate in seawater and the appropriate pressure of carbon dioxide in the atmosphere, which took place on the earth's surface during Mesozoic.

Wilson [14] notes the absence of dolomite on the surface of Recent marine sediments and its rare finds in the Holocene, as contrasted against its abundance in the geological past. Citing Adams, Rhodes, and other investigators, he describes the methods of dolomite formation, according to which a dense salt brine, where Mg/Ca ratio is increased due to Ca loss to gypsum and anhydrite precipitation caused by evaporation on tidal planes and lagoons, migrates downward, seeping through calcareous sediment and dolomitizes the latter. There is also the theory of reverse water movement (upward) as a result of evaporation suggested by Tszu and Seigenthaler. These investigators suggest this formation mechanism for Holocene dolomite found on evaporitic plains in the Persian Gulf and the Caribbean tropical region, in the surface crusts, and subsurface (up to 1.5 m) sediment zones formed during the past 3000 years.

Miller (cited by Chilingar et al. [16]) has described clear light-pink rhombic dolomite crystals (up to 0.14 mm) found in association with subidiomorphic aragonite and calcite grains in slurries of salt-evaporating plants. Teodorovich [13] suggests the possible dolomite formation in Recent environments.

The analysis of the literary sources thus suggests that the possibility of dolomite formation in Recent conditions is not ruled out, although it may be formed in small quantities compared with the Mesozoic period. Yet, on the scale of geological time, these processes can generate immense dolomite accumulations.

The existence of three types of dolomites formed by three different genetic routes has been established with certainty [10]. The first route is syngenetic (sedimentation): dolomites are formed by precipitation of dolomitic matter as fine-grained primary sediment in a high-salt basin, leading to extensive deposits consistent over large distances. The second route is metasomatic (according to Strakhov, sedimentary-diagenetic): Dolomites are formed by transport of originally precipitated dolomitic matter during the diagenesis. Strakhov refers to these dolomites, for example, the limestone-dolomite bed of the Upper Carboniferous in Samara meander loop. According to our data, we are inclined to place with this type also the Upper Callovian-Oxfordian dolomites, which are most widespread and consistent in Central and Northwestern Daghestan. The third route — epigenetic — is responsible for the dolomites formed by hydrothermal activity in an already existing rock.

The results of the study suggest that diagenetic dolomitization is common in carbonate rocks of the Upper Jurassic in Daghestan and is associated mainly with replacement processes. The original sedimentary-diagenetic Upper Callovian-Oxfordian dolomites, however, subsequently experienced various degrees of diagenetic alteration as a result of secondary (superimposed) processes. Their development was probably associated with the influx of magnesium in fluids, whose ions could spread to large distances, leading to diagenetic dolomitization of the sediment.

Kimmeridgian-Tithonian carbonate rocks of the gypsum-dolomite bed were dolomitized mainly in the same way as the subjacent rocks, by the syngenetic-diagenetic route. These rocks, however, contain thin (0.5-4 m) dolomite layers which are closer to diagenetic varieties by their characteristics. The formation of such dolomites found amid thick gypsum beds during the diagenesis was probably connected with dolomite-forming solutions penetrating into

suprajacent or subjacent layers of carbonate sediments when the gypsum beds experienced early diagenetic compaction. The influx of Mg^{2+} ions into carbonate sediments could be caused by reduction of sulfate ion [16] if Mg^{2+} was combined with SO_4^{2-} . The released Mg^{2+} ions could replace calcium, converting the sediment into diagenetic dolomite.

The partially replaced limestones identified in some of the profiles are probably attributable to a deficiency of magnesium, released during gypsum reduction, and also to the physical properties of the sediment rocks. This process resulted in all probability merely in the formation of disparate dolomite crystals, small spots, and accumulations, partial replacement of some authigenic minerals, and the consequent unequal degree of dolomitization of carbonate rocks.

* * *

The material presented in this paper suggests that the Late Jurassic, starting from the Callovian transgression, was associated with the influx of fine terrigenous matter, which continued through the end of the Middle Callovian. Somewhat later, during the Upper Callovian-Oxfordian and Kimmeridgian-Tithonian, the amounts of clay and silt became greatly reduced, and in the Northwestern Central and partly (for a short time) also Southern Daghestan, lagoon sedimentation settings were created; thick carbonate-sulfate and terrigenous sediments were then formed in marine, littoral-marine, and lagoon facies.

The hydrochemistry of the basin changed frequently, favoring the accumulation of diverse sedimentary types in the different parts of the basin, both in space and time. The chemical and mineral composition and the mechanical and structural-textural features of these rocks correlate closely with the paleogeographic environments of the region, which is important for finding and exploring mineral deposits.

The Upper Jurassic and Valanginian in Daghestan associate with numerous deposits and shows of limestone, dolomite, gypsum, sulfur, celestite, and authigenic mercury [15], as well as table salt, caustobiolite, oil and gas, thermal water, and brine. The practical importance of information about the diagenetic features of rocks is unquestionable, especially when these features are used to determine the occurrence patterns of primary and secondary porosity and permeability of rocks, essential for oil and gas production and hydrogeology, and for identifying the zones and abnormal concentration areas of products introduced by secondary processes as promising sites for prospecting and reconnaissance.

LITERATURE CITED

1. A. G. Aliev and A. M. Magomedov, *Lithology of Carbonate Deposits of the Upper Jurassic and Valanginian of Daghestan and North Azerbaidzhan* [in Russian], Elm, Baku (1972).
2. A. A. Baikov, I. V. Golikov-Zavolzhenskii, A. A. Golikova-Zavolzhenskaya, et al., "The origins of celestite in the North Caucasus," *Litol. Polezn. Iskop.*, No. 5, 77-86 (1978).
3. D. V. Drobyshev, *Gypsum in the Daghestan ASSR* [in Russian], Vol. 1, Izd. AN SSSR, Moscow (1935).
4. E. K. Depples, "Sandstone diagenesis," in: *Diagnosis and Catagenesis of Carbonate Rocks* [Russian translation], Mir, Moscow (1971), pp. 92-121.
5. I. A. Konyukhov, "Lithology of Mesozoic of the Eastern Ciscaucasia, in association with oil and gas prospects," *Tr. KOGE*, No. 3, 5-350 (1959).
6. G. K. Kerimov, T. G. Karchigaeva, and Yu. G. Mikolyuk, "Characteristics of the Upper Jurassic of Daghestan as connected with the exploration of carbonate deposits," *Tr. Inst. Geol. Dag. Filiala AN SSSR*, No. 5, 3-18 (1982).
7. G. P. Leonov and G. A. Loginova, "The main features of the geological history of Daghestan during the Upper Jurassic and Valanginian," *Uch. Zap. Mosk. Gos. Univ.*, No. 179, 87-103 (1956).
8. K. K. Magomedov, "The possibilities of lithologic classification of the Upper Jurassic and Valanginian," *Tr. Inst. Geol. Dag. Filiala AN SSSR*, No. 4(24), 177-189 (1980).
9. K. M. Sultanov, Ch. M. Khalifa-zade, and I. E. Efendiev, "Caustobiolitic bed in salt-bearing deposits of the Upper Jurassic in Daghestan," *Uch. Zap. Azerb. Inst. Ser. Geol.-Geogr.*, No. 6, 3-7 (1965).
10. N. M. Strakhov, "Facts and hypotheses in the formation of dolomite rocks," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 6, 3-22 (1958).
11. G. I. Teodorovich, *The Theory of Sedimentary Rocks* [in Russian], Gostoptekhizdat, Leningrad (1958).

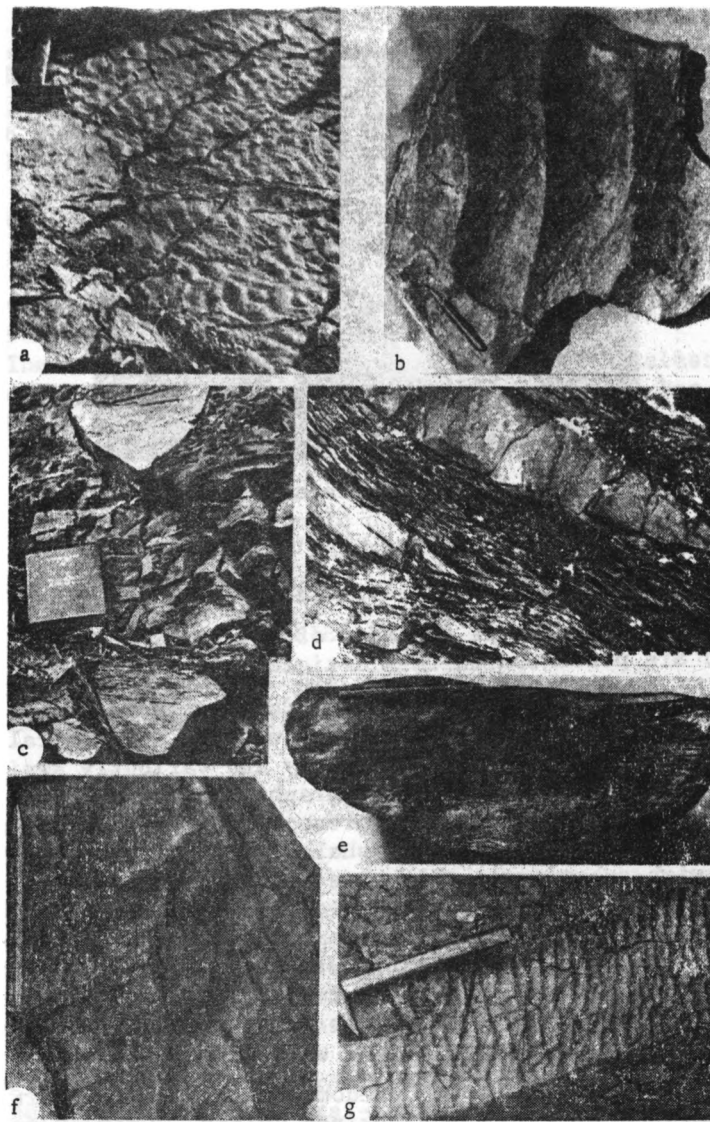


Fig. 2. Textural features of rocks from the Bederyshinsk subsuite of the Zil'merdaksk suite. a) Interference ripples on the bedding surface of red-colored siltstones (section along the Malyy Inzer River); b) large, symmetric, pointed-crest agitation ripples (section along the Malyy Inzer River); c-e) lenticular sandstone bodies amid fine-grained argillites: [c, d) section along the Katav River; e) section along the Yuryuzan' River]; f) casts with open desiccation cracks on the lower surface of sandstones (section along the Yuryuzan' River); g) symmetric sinusoidal dichotomizing agitation ripples on the surface of siltstones (section along the left bank of the Malyy Shishenyak River below the village of Bakeevo).

beds, wavy crossbeds, and wavy bedding, with the thickness of the series ranging from 5-7 cm. In reddish packets in a series of sections, the bedding surfaces of the siltstones and clay shales carry pseudomorphs of rock salt crystals. Packets of interbedded greenish-gray and gray colored siltstones with numerous channel scours are one of the interesting features of the Bederyshinsk subsuite (see Fig. 2c-e), which are characteristic of its upper horizons. Siltstones and silty argillites have thin parallel laminations and are represented, as shown by microscopic investigations, by weakly uncrystallized clay material, by finely lamellar hydromica with pale yellow and yellowish-orange interference colors, as well as by quartz. The content of silt size fragments of quartz and microcline reaches 15%. A characteristic

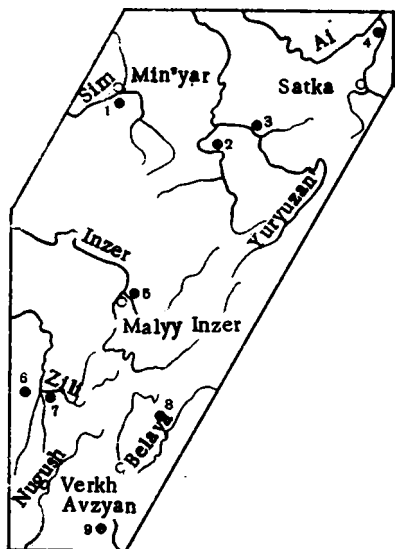


Fig. 3. Scheme of the distribution of the studied sections. 1) Chernaya River; 2) Katav River; 3) Yuryuzan' River; 4) village of Porogi; 5) Malyy Inzer River; 6) village of Khaibullino; 7) Zil'm River; 8) Kukhtur River; 9) Kal'tyagau River.

feature of rocks of this type is the significant quantity of glauconite in the ground mass of the argillites. Channel scours have the form of lenticular or wedge-shaped bodies whose size ranges from 15 cm (Fig. 2c) to 1.5 m (Fig. 2d), and they are formed of fine-grained sandstones or coarse-grained siltstones. Their lateral boundaries are seldom discordant in relation to the stratification of the surrounding rocks. Inside the lenses, the layering is thin, parallel to the upper boundary of the lens, or slightly sloping crossbeds in various directions, which intercut one another (Fig. 2e). Sometimes primary current lineations are observed by cleaving the lenses along the bedding. Authigenic glauconite is present in the sandstones and siltstones filling in the channel scours, in the same way as in the surrounding argillites.

The formation conditions for deposits of the Zil'merdaksk suite, which includes the Bederyshinsk subsuite, have been examined by many investigators. Garan' [2] assumed that deposits of Zil'merdaksk suite have a shallow water-marine genesis. A similar opinion is held by Akimova [1], taking into account the fact that sediments of Bederyshinsk times were formed in a moving shallow water-marine basin environment. Lungersgauzen [5] considered the Bederyshinsk subsuite deposits as littoral formations, alternating at the end of Zil'merdaksk time with sediments of salt lakes and lagoons. The deposits of the Zil'merdaksk suite are characterized on the whole as continental, which in Keller's opinion [3], explains the well-developed horizontal and crossbedding, the numerous ripple marks, and the desiccation cracks. Finally, Bekker, Feoktistov, Kutyrev, and a number of other authors consider the rocks of the Bederyshinsk subsuite, and the Zil'merdaksk suite as a whole, as deltaic deposits which accumulated in arid climatic conditions. Similar variations in the interpretation of the genesis of the Bederyshinsk subsuite rocks result primarily from the significant intermixing of the facies and the abrupt variability of the subsuite's structure from section to section.

In 1980-1983, the author collected a large amount of factual material which permitted renewed interpretation of the formation conditions for sediments of Bederyshinsk time. As a basis for investigation, the results of studying reference sections of the Bederyshinsk subsuite are incorporated into different structural-facies zones of the Bashkirsk mega-anticlinorium (Fig. 3). It is established that the terrigenous-carbonate deposits of Bederyshinsk subsuite may be related to three facies complexes (macrofacies), combining nine facies.

Facies Complex Deposits of a Semirestricted Coastal Marine Basin. The given complex is represented by facies of sand-silt-clay sediments from periodically flooded and drained sections of the coastal-marine plains (littoral zones) and facies of sand-silt-clay sediments from regions of intense underwater currents. The first facies combines various members of interbedded red and variegated sandstones, siltstones, and clay shales. Numerous fields of ripple marks, desiccation cracks, and halite pseudomorphs are correlated to the sediments of this facies.

Migrating ripples of the crossbed and wavy crossbed types are observed in the sand and silt interbeds. The intense red and cherry-red coloration of the rocks is explained by the significant admixture of finely dispersed hematite. In sections, the sediments of this facies

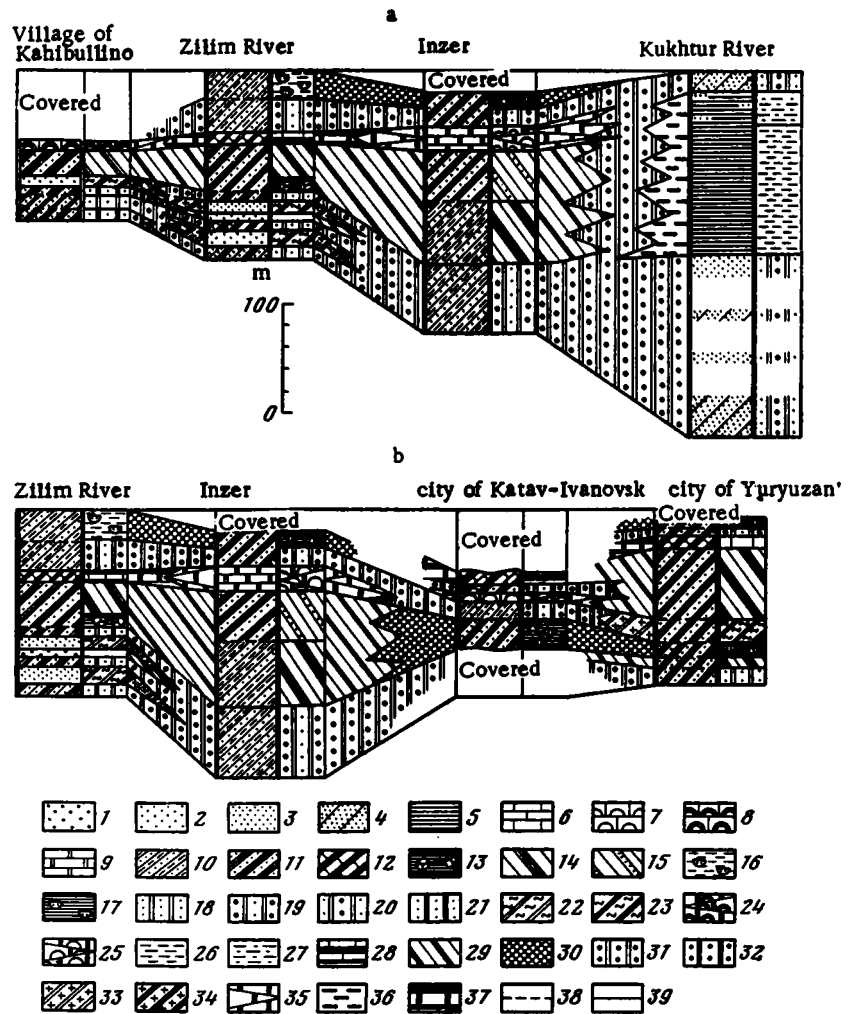


Fig. 4. Latitudinal (a) and submeridional (b) lithologic-facies profiles of deposits of the Bederyshinsk subsuite of the Zil'merdaksk suite. 1-3) sandstones: [1) coarse; 2) medium; 3) fine-grained]; 4) coarse-grained siltstones; 5) silty clay shales; 6) limestones; 7) limestones with indistinct organogenic structures; 8) stromatilitic limestones; 9) dolomites; 10-12) interbeds: [10) sandstones and siltstones; 11) sandstones and clay shales; 12) limestones and clay shales]; Genetic types of sediments: 13) interbedding of red-colored fine-grained sandstones, siltstones, and clay shales with numerous desiccation cracks and halite crystal pseudomorphs (PPL-1); 14) interbedding of red-colored fine-grained sandstones and clay shales with ripple marks and desiccation cracks (PPL-2); 15) interbedding of red-colored fine-grained sandstones and siltstones (PPL-3); 16) thinly laminated siltstones with lenticular sandstone bodies (PPT-1); 17) clay shales with lenticular sandstones bodies (PPT-2); 18) interbedding of fine-grained sandstones, siltstones, and clay shales (MMM-1); 19) interbedding of fine-grained sandstones and siltstones (MMM-2); 20) fine-grained sandstones or siltstones with horizontal bedding (MMM-3); 21) interbedding of fine-grained sandstones or siltstones and variegated clay shales (MMM_k-1); 22) medium-grained sandstones with crossbeds, wavy crossbeds, wavy bedding, and ripple marks (MMP-1); 23) variegated sandstones with crossbeds, cross-hatched bedding, ripple marks (MMP_k-1); 24) stromatolitic limestones (MMF-1); 25) nodular, brecciated limestones, with stromatolitic formations (MMF-2); 26) thinly horizontally laminated clay shales, fine-grained siltstones (MUT-1); 27) silty clay shales with siltstone interbeds and lenses (MUT-2); 28) interbedding of limestones and clay shales (MUP-1). Facies: 29) sand-silt-clay sediments of periodically flooded and drained parts of coastal-continental plains and littoral zones (PPL); 30) clay-silt-sand sediments from regions of intense underwater currents (PPT); 31) clay-silt-sand sediments from slightly moving shallow water (MMM); 32) red-colored clay-silt-sand sediments from a slightly moving shallow water marine basin (MMM_k); 33) sand sediments from a moving shallow water basin (MMP); 34) red-colored sand sediments of moving shallow water (MMP_k); 35) carbonate phytogenic sediments of moderately moving shallow water (MMF); 36) clay-silt sediments from remote parts of the basin (MUT); 37) clay-carbonate sediments from remote parts of the marine basin (MUP). Types of contacts: 38) gradual; 39) sharp.

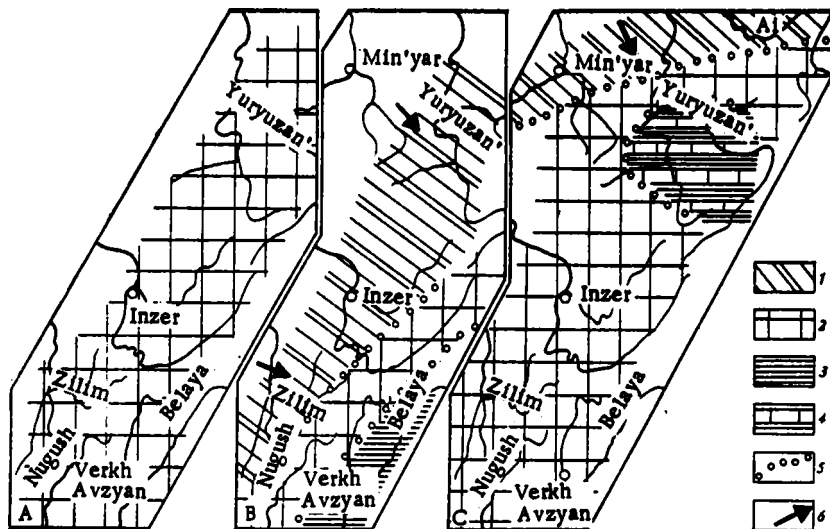


Fig. 5. Paleogeographic scheme for the beginning (A), middle (B), and end (C) of Bederyshinsk time. 1-4) Paleolandscape zones: [1) semirestricted coastal; 2) open moving shallow water marine basin; 3) open ocean with accumulation of fine terrigenous muds; 4) open ocean with accumulation of terrigenous-carbonate muds]; 5) boundaries of paleolandscape zones; 6) direction of clastic input.

are closely related to shallow water-marine deposits and sand-silt-clay sediments from regions of intense underwater currents (Fig. 4). The facies of the sand-silt-clay sediments from the regions of intense underwater currents are represented by two genetic types. To the first are attributed thinly, horizontally laminated siltstones of gray and greenish-gray color, with fine and coarse lenticular bodies of fine-grained sandstones, which form channel scour textures. Sediments of this type were observed in the upper part of the Bederyshinsk subsuite in a section on the Zilim River above the mouth of the Malyy Shishenyak (Little Shishenyak) River. The second genetic type of sediments includes greenish-gray clay shales and argillites, amid which are present coarse and/or fine "lenses" of fine-grained sandstones and siltstones. Sediments of this type are characteristic of the upper part of the subsuite in the section on the Malyy Inzer River, as well as those observed in proximity to the cities of Katav-Ivanovsk and Yuryuzan', where they occur in the upper and middle parts of Bederyshinsk subsuite. Apparently, the sediments of this facies are a connecting link between the shallow water deposits of open portions of the basin and the sediments of the littoral zone.

Facies Complex of Deposits of a Moving Shallow Water Marine Basin. This complex includes the sediments of five facies and has the widest distribution. The facies of a slightly moving shallow water marine basin is expressed by various sequences of fine-grained sandstones, siltstones, and clay shales. The ratio of detrital to clay rocks varies from 1:3 to 1:10. Two types of bedding systems are observed. The first bedding system is represented by sequences of various lithologic types of rocks, and the interbed thickness varies from 3-7 to 10-20 cm. The second bedding system is characteristic of the siltstones and sandstones. This is fine parallel or fine crossbeds and wavy crossbeds, with a series thickness of 3-10 cm. It is marked by differences in the grain size distribution of the layers, their composition, or coloration. Both laterally and in sections, the indicated facies is related to the sediments of semirestricted coastal shallow water and shallow water-marine deposits (see Fig. 4a).

The facies of variegated clay-silt-sand sediments of slightly moving marine shallow water is distinguished from the above-discussed facies by the coloration of the clay shales, which is due to the admixture of finely dispersed hematite. This facies has an insignificant distribution and is observed in sections at the city of Katav-Ivanovsk and in the basin of the Zilim River (village of Khaibullino).

The facies of sand sediments of moving shallow water are somewhat more widely distributed (Fig. 4b). These are represented by greenish-gray and variegated medium-grained sandstones with fine and medium-sized crossbeds, wavy crossbeds, and crosshatched bedding. The

thickness of a crossbed series reaches 25 cm. The sandstone bedding surfaces are often covered by wave and current ripple marks. The clastic sorting is good and moderately good. The primary grain form is angular-rounded or rounded. The indicated facies occur in association with the sediments of the first facies complex and shallow water-marine deposits of barely migratory portions of the basin. Their thickness varies from 7 to 25 m.

The facies of carbonate phytogenic sediments of barely and moderately moving shallow water are represented by gray and dark gray stromatolitic limestones, microphytolitic and nodular dolomites, as well as dolomites with indistinctly expressed organogenic structures. Their thickness in sections of the Bederyshinsk subsuite varies from 2 to 15 m. They have insignificant distribution in the western and central regions of the mega-anticlinorium, and they are completely absent in eastern subzone.

Complex of Deposits which are Remote from the Coastal Zones of the Marine Basin. The indicated complex unites two facies. The facies of clay-silt sediments which are remote from the coastal zones of the marine basin are represented by silty clay shales and/or fine-grained siltstones of greenish-gray and gray color with thin parallel laminations or massive form. In sections of the eastern limb of the Bashkirsk mega-anticlinorium, where deposits of this facies are related to shallow water-marine sediments, their thickness reaches 150-200 m (see Fig. 4a). The second facies, a component of the described complex, is represented by interstratification of massive or finely laminated limestones and/or dolomites with clay shales and siltstones, which apparently formed in zones of periodically interchanging carbonate and terrigenous sedimentation regimes under conditions of peaceful dynamics in the medium.

Analysis of the vertical and lateral distribution of the facies make it possible to restore the evolution of paleolandscapes at the end of Zil'merdaksk time in the territory of the modern Bashkirsk mega-anticlinorium. Apparently, at the start of Bederyshinsk time, zones of an open, migratory shallow water-marine basin existed in every territory of the Bashkirsk meganticlinorium (Fig. 5A), where sand-silt-clay and sand sediments were accumulated. In comparison with the end of the preceding Lemezinsk time, when the territory under consideration was represented by alternation of shallow water-marine and littoral zones, some widening of the marine water area occurred in this period. Subsequently, in the middle of Bederyshinsk time, and possibly somewhat earlier in the north, pronounced differentiation of the landscape zones is observed (see Fig. 5B). In the central and western portions of the mega-anticlinorium, which apparently transformed into a flat coastal-continental plain periodically flooded by the ocean, red and green colored siltstones and silt-sand-clay sediments were formed, in high and low tidal zones, ephemeral lakes, and semirestricted bays and lagoons. This region was bordered to the southeast by a narrow band of shallow marine water and a zone of open ocean, where the accumulation of fine terrigenous muds predominated. A large regression of the marine basin is apparently correlated to this time interval. A few changes in the positions of the landscape zones occurred toward the end of Bederyshinsk time (see Fig. 5C). A region of open shallow water, which earlier extended from the headwaters of the Bolshoi Inzer (Great Inzer) River to the southwest, significantly widened, and enveloped almost all the territory of the Bashkirsk uplift. The region of semirestricted coast was probably preserved only in the north. At this time, fine terrigenous and chemogenic carbonate muds accumulated in the basin of the Yuryuzan' and Katav Rivers.

Thus, the obtained data make it possible to consider the Bederyshinsk subsuite of the Zil'merdaksk suite as a polyfacies complex of sediments with a complicated structure. In the western and central regions of the Bashkirsk mega-anticlinorium, shallow water-marine and coastal-continental sedimentation processes predominated during the entire extent of Bederyshinsk time. Stable marine sediment accumulation took place only in the eastern zone. The middle of Bederyshinsk time was signaled by a significant reduction in the area of the marine basin. The beginning of a pronounced aridization of the climate is related to this interval, which subsequently led to the formation of the thick red-colored carbonate deposits of the Katavsk suite. In comparison with the initial stages in the development of the Late Riphean sedimentation basin (Bir'yansk time), when the predominant accumulation was of sand-gravel and sand-silt sediments, from alluvial, alluvial-deltaic, and coastal-continental genesis [6], Bederyshinsk time was characterized by a gradual increase in the role of sediments from the open and semirestricted coast of the marine basin and shallow water-marine sand-silt-clay formations.

LITERATURE CITED

1. G. N. Akimova, "Crossbedding in the rocks of the Zil'merdaksk suite in the Southern Urals," in: Materials on the Stratigraphy and Tectonics of the Urals, Tr. Vses. Nauchn. Issled. Geol. Inst., Nov. Ser., 144, 36-65 (1967).
2. M. I. Garan', On the Age and Formation Conditions of Ancient Suites of the Western Slope of the Sothern Urals [in Russian], Gosgeoltekhizdat, Moscow (1946).
3. B. M. Keller, "On Riphean formations (Eniseisk ridge, Southern Urals)," Izv. Akad. Nauk SSSR, Ser. Geol., No. 7, 99-107 (1970).
4. V. I. Kozlov, The Upper Riphean and Vendian of the Southern Urals [in Russian], Nauka, Moscow (1982).
5. G. F. Lungersgauzen, "On the facies nature and the deposition conditions of ancient suites of the Bashkir Urals (Lipalisk system in the Southern Urals)," in: Sov. Geol., No. 18, 35-74 (1947).
6. A. V. Maslov, "Lithologic-facies features of Upper Riphean deposits of the Southern Urals. Communication I. Formation conditions of terrigenous complexes of the Bir'yansk subsuite of the Zil'merdaksk suite," Litol. Polezn. Iskop., No. 6, 110-121 (1985).
7. A. I. Olli, Ancient Deposits of the Western Slope of the Urals [in Russian], Izd. SGU, Saratov (1948).
8. V. A. Romanov, Type Sections of the Precambrian in the Southern Urals [in Russian], Nauka, Moscow (1973).
9. H. E. Reineck and I. B. Singh, Depositional Sedimentary Environments (With Reference to Terrigenous Clastics), 2nd edn., Springer-Verlag (1975).
10. Riphean Stratotypes. Stratigraphy. Geochronology, Tr. Geol. Inst. Akad. Nauk SSSR, 377 (1983).
11. P. P. Timofeev, V. N. Kholodov, and I. V. Khvorova, "Evolution of sediment accumulation processes on continents and in oceans," Litol. Polezn. Iskop., No. 5, 3-23 (1983).
12. A. Chandhuri, "Influence of eolian processes on Precambrian sandstones of the Godavary Valley, South India," Precambrian Res., 4, No. 4, 339-360 (1977).
13. R. L. Folk, "Bimodal supermature sandstones: product of the desert floor," Proc. XXIII Intern. Geol. Congr., 8, 9-32 (1968).

METHODS

A MEANS OF SAMPLING SUSPENDED SEDIMENTS IN BOTTOM WATERS ON ANY PART OF THE SHELF

R. D. Kos'yan and A. P. Filippov

UDC 551.463.8:551.35

Measurement of flow characteristics of suspended sediments is important in the study of movement of lithospheric material on the continental shelf. Quantitative information on the movement of near-bottom clastic material is of considerable scientific and practical interest for geologists, geomorphologists, and hydrologists. Modern measurement techniques, however, do not yet satisfy the requirements of investigators.

Direct methods of measurement (optical, radiometric, acoustical, conductometric, etc.) are widely used in the laboratory, where calculation of the particles or recording of any changes in the characteristics of the aqueous medium associated with the presence of suspensions are carried out directly in the current. These methods are, however, inadequate when applied to marine conditions [2].

It is recommended in [4] that, for obtaining information on the movement of suspended sediments, only bathymetric sampling methods, instantaneous operation and continuous filling, be used. The correct application of this method depends on the use of booms, mooring hawsers, overhead trolleys, etc.

Southern Branch, P. P. Shirshov Institute of Oceanology, Academy of Sciences of the USSR, Gelendzhik. Translated from *Litologiya i Poleznye Iskopaemye*, No. 3, pp. 135-137, May-June, 1986. Original article submitted June 20, 1984.

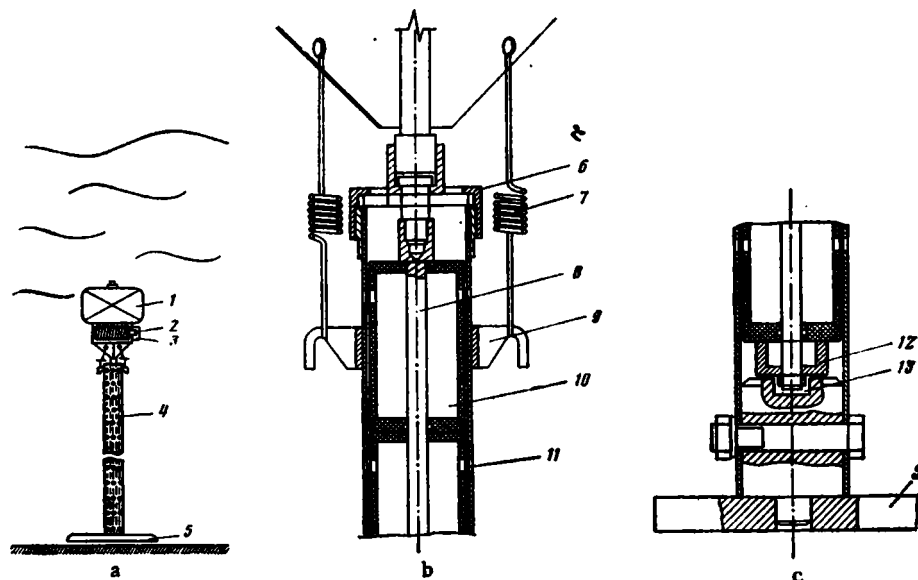


Fig. 1. Diagram of measuring station. a) General view, b) upper part of body, c) lower part. 1) Buoy, 2) reel, 3) hydro-acoustic breaker, 4) body, 5) weight, 6) end cap, 7) coil spring, 8) internal shaft, 9) hook, 10) bathymeter-sediment accumulator, 11) intake, 12) bearing ring, 13) housing for time delay mechanism.

Thus, in order to obtain data that can be used on the sediment regime in a given body of water, a fixed structure is necessary. Obviously, this requirement seriously restricts the possibilities for observation. The other method recommended (working from a floating facility) is also ineffective, since it does not permit some of the most important observations, those during storms.

Independent stations, rigged from bathymetry and sediment capture, have been widely used in recent field studies [1]. Their use makes it possible to obtain information on the distribution of suspended sediments in the water column and along a profile of marine coastal zones. Obvious advantages of this method are its simplicity, reliability, and the ability to obtain simultaneous data over a large body of water. At the same time, the use of these measuring stations limits the depth of observation, since maintenance requires costly and not always safe diving work. Therefore, measurements with the use of sediment accumulators are carried out only on the upper part of the shelf. Only a small amount of data is available on the lower shelf, and it only applies to periods of calm weather.

Using the independent station with the bathymeter-accumulator as a basis, the authors have developed a device that makes it possible to obtain adequate information on the vertical distribution and composition of suspended sediment in near-bottom waters on any part of the shelf and under any hydrometeorological conditions [3].

In developing the measuring device, which would be able to operate without the help of a diver and at relatively large depths, it was necessary to consider the following points.

1. On contact of the measuring station with the bottom, mud is generally stirred up which falls into the sediment accumulator and can distort the picture of suspended sediment distribution. Therefore, opening of the accumulator should take place after some delay beyond arrival.

2. On ascent of the open accumulator, partial or complete removal of the solid particles in it can take place.

3. The measuring station should be independent and able to make measurements during long periods under very different hydrodynamic regimes.

4. The surface buoy, having a certain sail effect, in strong waves can tug at and even overturn the measuring station.

5. The buoys located far from shore may be snagged by fishermen, or caught and ripped off by passing ships. On long exposure, it cannot be ruled out that the rope connecting the measuring station to the marker buoy will wear out.

We have taken all these points into account in our proposed construction of a measuring station.

The station, a general view of which is shown in Fig. 1a, contains a bathymeter-accumulator cassette with radial through-holes; cylindrical body 4 with weight 5 at the base; reel 2 with cable and hydroacoustic breaker 3 attached to body with buoy rope for connection to buoy 1. The height of the station is selected according to the conditions of the experiment and the thickness of the near-bottom zone in which distribution of suspended sediment is to be studied.

The buoyancy of the buoy P_1 should be set so that P_1 exceeds the weight of the station P_2 less the ballast weight P_3 . The magnitude of P_2 will depend on the height of the station, but in any case should fulfill the condition $P_1 < P_2 + P_3$. The station will then attain a vertical position on the bottom. In case the ballast weight breaks away from the body for some unforeseen reason, the buoy will draw the measuring device to the surface, where there is a chance it will be seen by the monitor ship. The buoy size should be determined by the assigned buoyancy.

The sediment accumulator cassette 10 is assembled with the bathymeter on the shaft 8 and inserted into the body (see Fig. 1b). Round intake holes 11 are located around the surface of the cylinder at equal spacings from one another. Free movement of the cassette within the body is limited above by the end cap 6 and below (see Fig. 1c) by the bearing ring 12. The instrument is held in working position and is compensated for the buoyancy of the buoy by the coil springs 7, which also ensures that the accumulator is held fully open throughout its exposure.

A time delay for the opening of the accumulator intakes is provided for. A solid substance, pressed into a certain shape, is placed in the housing 13 for this purpose; when subjected to seawater it either dissolves, corrodes, or gains viscosity over a certain period of time as determined by specifications of the experiment. This material may be sugar, magnesium, clay, etc.

The ballast weight 5, fastened to the base of the body, together with the buoy 1 serves to keep the instrument in a vertical position. The ballast weight P_3 should be selected according to the assumed local velocity of current or wave motion and nature of the bottom. In order for the station to be stable, the frictional force on the bottom must exceed any possible drag. Thus, the condition

$$K(P_2 + P_3 - P_1) > C_x S_0 \frac{\rho v^2}{2},$$

must be met, where K is the coefficient of friction of the weight on the bottom, S_0 is the cross-sectional area perpendicular to the direction of pressure, v is the current velocity, ρ is the density of the liquid, and C_x is the drag coefficient of the body, depending on the value of the Reynolds number.

In lieu of experimental data on current velocity and bottom conditions, the values of C_x and K can be determined from a handbook in order to calculate the value of P_1 . It is recommended that this measuring device be used at relatively great depths, where mainly pelitic and silty particles of the sea bottom pass into a suspended state. The concentration gradient of fine suspended matter in this zone is generally constant [1] and, thus, the size of the bottom weight would not have a significant effect on the vertical distribution of the suspended matter.

After assembly, the measuring station is positioned on the bottom at the locality selected by catching a cable ring on hook 9 and the use of a small handle or ship's winch. When bottom is reached, the tension on the cable is relaxed and the cable ring easily slips off. After a given time interval, the delaying substance dissolves and the bathymeter-accumulator cassette drops down by the action of the coil spring and its own weight. The bathymeter openings match the intake openings of the body, and the measuring station is ready to gather information. On completion of the exposure time, a signal is sent from the ship to the hydroacoustic breaker, which releases the buoy. The buoy, floating upward, unwinds the cable from the barrel of the reel, which should be rigged with a brake to ensure even unwinding.

The brightly colored buoy is easily spotted on the surface. The measuring station is taken aboard the ship by means of the cable, which is fastened to the bathymeter-accumulator cassette. In the process, the body drops down under its own weight and closes the intake holes. This prevents leakage of the sample during the ascent.

This measuring station retains essentially all of the positive qualities of the independent stations with accumulators [1]. However, its use precludes the need for diving work, which recommends it for use on any part of the shelf. Another advantage of the station is the absence of a marker buoy at the surface during its period of exposure. It can be set up for long periods of time, considering that collection of information takes place only during strong hydrodynamic disturbances. During calm weather, the horizontal aspect of the intake holes prevents the entry of solid particles into the bathymeter housing.

Similar measuring devices could be used for study of sediment dynamics in submarine canyons, turbidity currents, or the effect of currents on the redistribution of bottom sediments on the shelf. They could be used to test the hypothesis that turbulent diffusion plays a leading role in the transport of clastic material from the margins to the central areas of the oceans. The collection of field data makes it possible to resolve many general, regional, and practical problems of lithodynamics.

It should be noted that although this article deals with the use of the measuring station on the continental shelf, this technology can be applied to other zones of the ocean as well.

LITERATURE CITED

1. S. M. Antsyferov and R. D. Kos'yan, Recommended Methods for the Study of Suspended Sediments on the Upper Part of the Shelf [in Russian], Inst. Okeanol. Akad. Nauk SSSR, Moscow (1980).
2. S. M. Antsyferov, R. D. Kos'yan, and É. L. Onishchenko, "A method of natural study of the movement of suspended clastic material," *Okeanol.*, 15, No. 2, 296-301 (1975).
3. R. D. Kos'yan and A. P. Filippov, "A device for sampling suspended sediments in the bottom layer on a marine shelf," Inventor's Certificate, No. 855441, Byull. Izobret., No. 30 (1981).
4. Handbook on Methods of Study and Calculation of Movement of Sediment and Coastal Dynamics for Engineering Research [in Russian], Gidrometeoizdat, Moscow (1975).

CHANGING YOUR ADDRESS?

In order to receive your journal without interruption, please complete this change of address notice and forward to the Publisher, 60 days in advance, if possible.

(Please Print)

Old Address:

name

address

city

state (or country)

zip code

New Address

name

address

city

state (or country)

zip code

date new address effective

name of journal

THE LANGUAGE OF SCIENCE
Plenum
PUBLISHING CORPORATION

233 Spring Street, New York, New York 10013

MEASUREMENT TECHNIQUES*Izmeritel'naya Tekhnika*

Vol. 29, 1986 (12 issues) \$645

MECHANICS OF COMPOSITE MATERIALS*Mekhanika Kompozitnykh Materialov*

Vol. 22, 1986 (6 issues) \$545

METAL SCIENCE AND HEAT TREATMENT*Metallovedenie i Termicheskaya Obrabotka Metallov*

Vol. 28, 1986 (12 issues) \$675

METALLURGIST*Metallurg*

Vol. 30, 1986 (12 issues) \$645

PROBLEMS OF INFORMATION TRANSMISSION*Problemy Peredachi Informatsii*

Vol. 22, 1986 (4 issues) \$495

PROGRAMMING AND COMPUTER SOFTWARE*Programmirovaniye*

Vol. 12, 1986 (6 issues) \$225

PROTECTION OF METALS*Zashchita Metallov*

Vol. 22, 1986 (6 issues) \$595

RADIOPHYSICS AND QUANTUM ELECTRONICS*Izvestiya Vysshikh Uchebnykh Zavedenii, Radiofizika*

Vol. 29, 1986 (12 issues) \$645

REFRACTORIES*Ogneupory*

Vol. 27, 1986 (12 issues) \$595

SIBERIAN MATHEMATICAL JOURNAL*Sibirskii Matematicheskii Zhurnal*

Vol. 27, 1986 (6 issues) \$795

**SOIL MECHANICS AND
FOUNDATION ENGINEERING***Osnovaniya, Fundamenty i Mekhanika Gruntov*

Vol. 23, 1986 (6 issues) \$585

SOLAR SYSTEM RESEARCH*Astronomicheskii Vestnik*

Vol. 20, 1986 (4 issues) \$425

SOVIET APPLIED MECHANICS*Prikladnaya Mekhanika*

Vol. 22, 1986 (12 issues) \$645

SOVIET ATOMIC ENERGY*Atomnaya Energiya*

Vols. 60-61, 1986 (12 issues) \$695

**SOVIET JOURNAL OF GLASS PHYSICS
AND CHEMISTRY***Fizika i Khimiya Stekla*

Vol. 12, 1986 (6 issues) \$295

**SOVIET JOURNAL OF
NONDESTRUCTIVE TESTING***Defektoskopiya*

Vol. 22, 1986 (12 issues) \$775

SOVIET MATERIALS SCIENCE*Fiziko-khimicheskaya Mekhanika Materialov*

Vol. 22, 1986 (6 issues) \$565

SOVIET MICROELECTRONICS*Mikroelektronika*

Vol. 15, 1986 (6 issues) \$325

SOVIET MINING SCIENCE*Fiziko-tehnicheskie Problemy Razrabotki**Poleznykh Iskopaemykh*

Vol. 22, 1986 (6 issues) \$645

SOVIET PHYSICS JOURNAL*Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika*

Vol. 29, 1986 (12 issues) \$645

**SOVIET POWDER METALLURGY AND
METAL CERAMICS***Poroshkovaya Metallurgiya*

Vol. 25, 1986 (12 issues) \$695

STRENGTH OF MATERIALS*Problemy Prochnosti*

Vol. 18, 1986 (12 issues) \$795

THEORETICAL AND MATHEMATICAL PHYSICS*Teoreticheskaya i Matematicheskaya Fizika*

Vol. 66-69, 1986 (12 issues) \$625

UKRAINIAN MATHEMATICAL JOURNAL*Ukrainskii Matematicheskii Zhurnal*

Vol. 38, 1986 (6 issues) \$625

Send for Your Free Examination Copy

Plenum Publishing Corporation, 233 Spring St., New York, N.Y. 10013
In United Kingdom: 88/90 Middlesex St., London E1 7EZ, England

Prices slightly higher outside the U.S. Prices subject to change without notice.

RUSSIAN JOURNALS IN THE PHYSICAL AND MATHEMATICAL SCIENCES

AVAILABLE IN ENGLISH TRANSLATION

ALGEBRA AND LOGIC

Algebra i Logika
Vol. 25, 1986 (6 issues) \$445

ASTROPHYSICS

Astrofizika
Vols. 24 and 25, 1986 (6 issues) \$545

AUTOMATION AND REMOTE CONTROL

Avtomatika i Telemekhanika
Vol. 47, 1986 (24 issues) \$795

COMBUSTION, EXPLOSION, AND SHOCK WAVES

Fizika Goreniya i Vzryva
Vol. 22, 1986 (6 issues) \$565

COSMIC RESEARCH

Kosmicheskie Issledovaniya
Vol. 24, 1986 (6 issues) \$645

CYBERNETICS

Kibernetika
Vol. 22, 1986 (6 issues) \$565

DIFFERENTIAL EQUATIONS

Differentsial'nye Uravneniya
Vol. 22, 1986 (12 issues) \$645

DOKLADY BIOPHYSICS

Doklady Akademii Nauk SSSR
Vol. 286-291, 1986 (2 issues) \$185

FLUID DYNAMICS

Izvestiya Akademii Nauk SSSR, Mekhanika Zhidkosti i Gaza
Vol. 21, 1986 (6 issues) \$640

FUNCTIONAL ANALYSIS AND ITS APPLICATIONS

Funktsional'nyi Analiz i Ego Prilozheniya
Vol. 20, 1986 (4 issues) \$495

GLASS AND CERAMICS

Steklo i Keramika
Vol. 43, 1986 (12 issues) \$695

HIGH TEMPERATURE

Teplofizika Vysokikh Temperatur
Vol. 24, 1986 (6 issues) \$645

HYDROTECHNICAL CONSTRUCTION

Gidrotekhnicheskoe Stroitel'stvo
Vol. 20, 1986 (12 issues) \$475

INDUSTRIAL LABORATORY

Zavodskaya Laboratoriya
Vol. 52, 1986 (12 issues) \$645

INSTRUMENTS AND EXPERIMENTAL TECHNIQUES

Pribory i Tekhnika Éksperimenta
Vol. 29, 1986 (12 issues) \$745

JOURNAL OF APPLIED MECHANICS AND TECHNICAL PHYSICS

Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki
Vol. 27, 1986 (6 issues) \$675

JOURNAL OF APPLIED SPECTROSCOPY

Zhurnal Prikladnoi Spektroskopii
Vols. 44-45, 1986 (12 issues) \$675

JOURNAL OF ENGINEERING PHYSICS

Inzhenerno-fizicheskii Zhurnal
Vols. 50-51, 1986 (12 issues) \$675

JOURNAL OF SOVIET LASER RESEARCH

A translation of articles based on the best Soviet research in the field of lasers
Vol. 7, 1986 (6 issues) \$245

JOURNAL OF SOVIET MATHEMATICS

A translation of Itogi Nauki i Tekhniki and Zapiski Nauchnykh Seminarov Leningradskogo Otdeleniya Matematicheskogo Instituta im. V. A. Steklova AN SSSR
Vols. 32-35, 1986 (24 issues) \$1,345

LITHOLOGY AND MINERAL RESOURCES

Litologiya i Poleznye Iskopaemye
Vol. 21, 1986 (6 issues) \$645

LITHUANIAN MATHEMATICAL JOURNAL

Litovskii Matematicheskii Sbornik
Vol. 26, 1986 (4 issues) \$325

MAGNETOHYDRODYNAMICS

Magnitnaya Gidrodinamika
Vol. 22, 1986 (4 issues) \$495

MATHEMATICAL NOTES

Matematicheskie Zametki
Vols. 39-40, 1986 (12 issues) \$645

continued on inside back cover